

# Research for High Concentration of Precious Metal and Thin Layer of Catalyst Top Layer

Syouji INOSE\*

Tatsuya OKAYAMA\*

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## ABSTRACT

Reduction of the precious metal loading of a catalyst generally causes a decline in light-off performance.

Study of the low temperature reaction mechanism of catalysts indicated the importance of the top layer in the reaction, thus increasing reactivity in the top layer was established as an objective. The concentration of precious metals in the top layer was increased, and the thickness of the layers was reduced. At the same time, the precious metal loading of the bottom layer, which contributes little to light-off performance, was reduced by 80%. However, increasing the concentration of precious metals in the top layer caused a reduction in performance due to a sintering effect between the metals. Research was therefore conducted on the employment of a high-thermostability support material (alumina) to control the sintering.

This research has enabled the development of a three-way catalyst with significantly reduced precious metal loading while retaining conversion performance equivalent to that of conventional catalysts.

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## 1. Introduction

The tightening of automotive emissions regulations has recently been increasing globally, as seen in the Tier-2 and LEV2 regulations in the US, EURO4 regulations in the EU, and 2005 regulations in Japan.

Catalyst conversion performance plays an important role in reducing emissions, enabling manufacturers to respond to the tightening regulations. Conversion performance is strongly dependent on the precious metal loading of the catalyst, and therefore the amount of precious metals used per vehicle has tended to increase with tightening regulations.

The majority of automotive emissions occur immediately after engine starts, before the catalyst has warmed up. Achieving enhanced light-off performance is therefore important in terms of

reducing overall emissions. However, light-off performance generally declines when precious metal loading is reduced.

The research project discussed in this paper considered the relationship between precious metal loading and light-off performance theoretically from the perspective of the catalytic reaction mechanism. Based on these considerations, research was focused on minimizing precious metal loading while maintaining conversion performance equivalent to that of conventional catalysts.

## 2. Development Goals

### 2.1. Emissions Characteristics

Figure 1 shows the results of measurements of hydrocarbon (HC) emissions from the 2003 model Accord (in-line 4-cylinder

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\* Tochigi R&D Center

2.4L engine) under testing in FTP LA-4 mode<sup>(1)</sup>. The 2003 Accord cleared the PZEV regulations, the most stringent in the US.

Of the various emission components, carbon monoxide (CO), Hydrocarbon (HC) and nitrogen oxides (NOx), it is HC that presents the greatest challenge in clearing regulation targets. In the test cycle shown in Fig. 1, Bag-1 represents the cycle which follows engine start, while Bag-2 and Bag-3 are hot cycles, i.e. they occur after the engine has warmed up. Approximately 80% of total HC emission occurs in Bag-1. This is due to advances in air-fuel ratio control systems<sup>(2)</sup> and enhancements in catalyst characteristics which have enabled contemporary emissions conversion systems to significantly reduce emissions in Bag-2, 3 where the catalyst is activated after the engine has warmed up.

To achieve further emissions reductions in the future, it will therefore be necessary to reduce emissions in Bag-1 at engine start, and early activation of the catalyst will be essential in enabling this.

## 2.2. Emissions Reduction Technologies

Both rapid heating of the catalyst by means of engine management<sup>(3)</sup> and close coupled positioning of the catalyst are currently employed to achieve early activation of conventional catalysts. In addition, research has been conducted on the following catalyst types to enhance light-off performance and reduce HC emissions:

- (1) Zone coat catalysts, in which the precious metal loading is increased at the exhaust gas entrance<sup>(4)</sup>
- (2) Catalysts employing complex oxide catalysts (perovskite structures, etc.) to supplement precious metals<sup>(5), (6)</sup>
- (3) Transient adsorption of the pre-activation HC emittants<sup>(7)</sup>

However, to clear increasingly stringent future emissions regulations and reduce cost, research on methods of making maximally effective use of the precious metals in the catalyst is required.

## 2.3. Issues of Conventional Catalysts

For activation, a catalyst must be heated to their respective functional temperatures (activation temperature) or above. The catalyst is heated by heat exchange with exhaust gases. When the engine is stopped, the temperature of the catalyst equilibrates to ambient temperature; after engine start, the catalyst is heated to activation temperature by the temperature of exhaust gases. However, until the activation temperature is reached, exhaust gases are emitted without catalytic conversion. Low temperature light-off performance is therefore essential in a catalyst.

Figure 2 shows the relationship between precious metal loading and light-off performance in a conventional catalyst. Conventional catalysts present the issue that reducing precious metal loading causes light-off performance to decline.

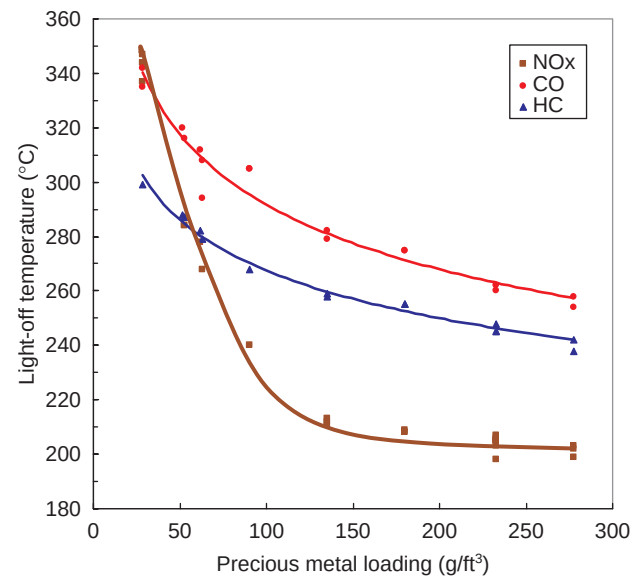


Fig. 2 Relationship between loading of precious metal and light-off temperature

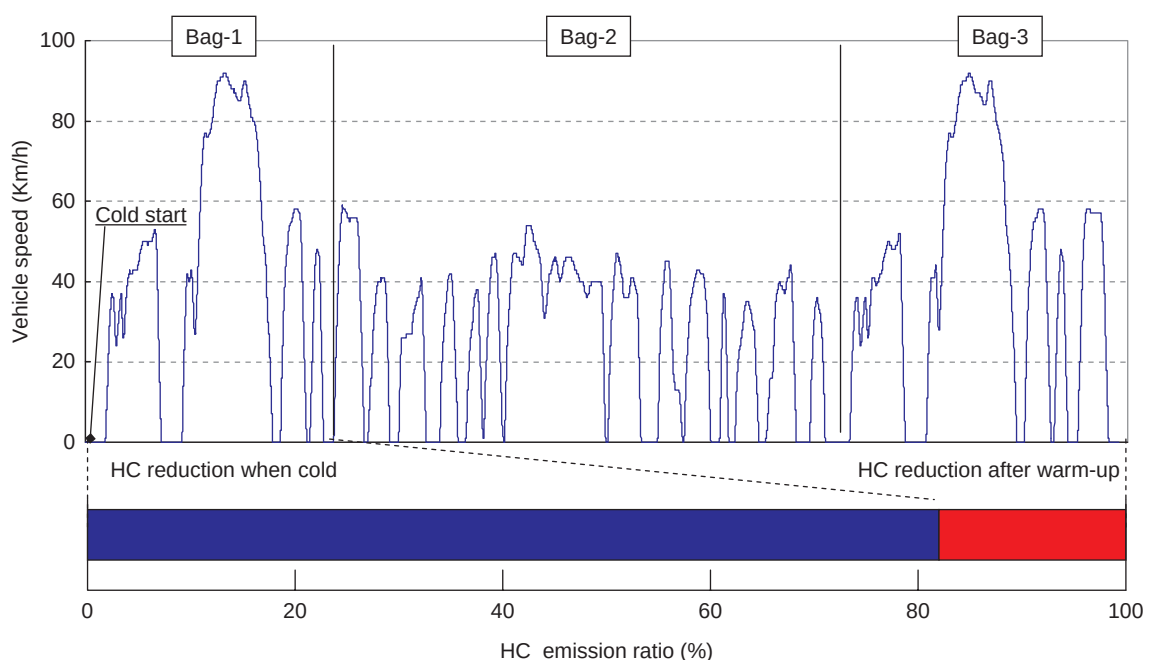


Fig. 1 HC emission in the cold condition and after warm-up (US LA-4 test cycle)

Theoretical consideration of the relationship between precious metal loading and light-off performance, from the perspective of the catalyst reaction mechanism, led to the establishment of the target of the project discussed here as the development of a catalyst that displays identical light-off performance to that of a conventional catalyst with half the precious metal loading.

### 3. Theory

#### 3.1. Theory of Catalyst Reaction

Here, the authors conduct a simple theoretical examination of catalytic reactions on solid surfaces to investigate methods of effectively utilizing the precious metals in the top layer of the catalyst, to enhance light-off performance.

The following two factors are important in the chemical reaction:

- (1) Activation energy, which forms an energy barrier for reaction
- (2) Molecular energy, which crosses the energy barrier for reaction, to cause a reaction

The development process of chemical industrial catalysts focuses on (1), and generally changes the active species to reduce activation energy. However, from the perspective of durability and conversion performance, no active species have been discovered that can supplant the precious metals platinum (Pt), palladium (Pd) or rhodium (Rh) which are used in current automotive three-way catalysts. Therefore, this project focused on (2). With the aim of achieving enhanced light-off performance, a scenario in which high-temperature exhaust gas was introduced to a room temperature catalyst was assumed, and activity at the atomic and molecular levels was studied using classical molecular collision theory without considering quantum effects.

#### 3.2. Molecular Collision Theory on a Solid Surface

Molecular collision theory is effective in dealing with reactions in the gas phase. This project applied this classical theory to a system including solid catalyst surfaces to determine a method of effectively utilizing the energy in the system.

In molecular collision theory, the essential condition for a reaction to occur is that the translational energy generated by molecular collisions exceeds activation energy. We will use this theory to consider reactions on solid catalyst surfaces. When the molecules making up exhaust gas are absorbed by a solid catalyst surface, translational energy is transformed into surface free energy. The essential condition for a reaction to occur is for the sum of the transformed energy and the energy in the solid surface system to be greater than that of the activation energy ( $E_a$ ) of the catalyst. Based on these considerations, we will apply molecular collision theory to solid catalyst surfaces to study methods of achieving enhanced light-off performance.

#### 3.3. Modification of Catalyst to Reduce Light-off Temperature

##### 3.3.1. Application of molecular collision theory to solid surface

Assuming that the temperature of the catalyst is sufficiently low in relation to the temperature of the exhaust gas, the energy required for a reaction to proceed is mainly imparted by the translational energy of the gas phase molecules. The reaction is therefore largely determined by the magnitude of the translational kinetic energy of

the molecules in the gas phase, and can be theorized as follows: The gas molecules impart surface free energy to the catalyst through collisions, but the essential condition for a reaction to proceed is that the translational energy is greater than  $E_a'$ , the sum of the activation energy of the parts of the catalyst involved in the reaction ( $E_a$ ), and the energy imparted to the surface free energy of the parts not involved in the reaction.

The distribution of molecular velocity in the gas phase is dependent on temperature, and can be expressed as the following Maxwell-Boltzmann distribution:

$$\frac{dN}{N} = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left( -\frac{mv^2}{2kT} \right) v^2 dv \quad (1)$$

$N$  : Total number of molecules

$v$  : Velocity of molecules

$m$  : Mass of molecules

$k$  : Boltzmann constant

$T$  : Temperature

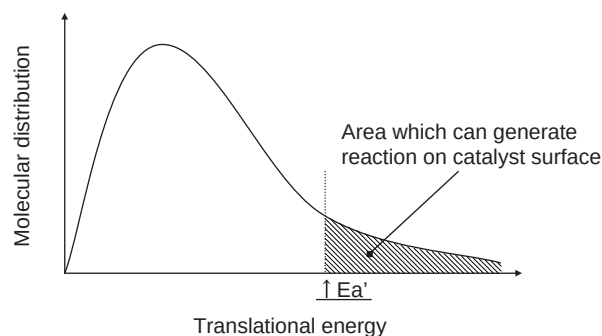
$dN$  : Number of molecules with velocities between  $v$  and  $dv$

This equation enables the velocity distribution of the molecules, and also the energy distribution in the gas molecules, to be obtained. Figure 3 shows the relationship between the distribution of translational energy and the translational energy equivalent to  $E_a'$ , which can enable a chemical reaction to proceed on the solid catalyst surface, in the gas molecules. As the diagram shows, although average molecular energy is low, there are molecules in the system that can enable a reaction. Based on the theory discussed above, the mechanism is as follows: Molecules with a translational energy greater than  $E_a'$ , i.e. that satisfy the conditions for a reaction, collide with the solid surface and their translational energy is transformed into surface free energy. If the conditions for a reaction are satisfied, the reaction will then proceed. It is therefore important to effectively exploit these small numbers of molecules that enable a reaction to proceed in order to ensure low-temperature reactions in the catalyst. We will look at two scenarios from the perspective of developing a method of effectively exploiting the molecules with energy levels greater than that of  $E_a'$ :

- (1) Molecular collisions cause a reaction to proceed
- (2) A reaction does not proceed despite molecular collisions

##### 3.3.2. Scenario (1)

We will look first at scenario (1), in which the collision of molecules with a translational energy greater than  $E_a'$  satisfies the



$E_a'$  : Translational energy distribution of gas molecules which can provide energy for reaction on catalyst surface

Fig. 3 Translational energy distribution of molecules

conditions for reaction and the reaction proceeds on the surface of the catalyst.

Exhaust gas conversion reactions are generally exothermic; as the reaction proceeds, reaction energy is imparted to surface free energy. Some of this surface free energy is lost through molecular desorption or as translational energy, but the area in which the reaction is taking place continues to possess a higher energy level than that of its surrounding areas. As the surface free energy of the solid catalyst increases, even molecules with a translational energy lower than  $E_a'$  will satisfy the conditions for reaction, enabling the reaction to propagate. In other words, maintaining the surface free energy of the area of the catalyst in which the reaction has occurred is important in enhancing light-off performance.

As time elapses, the imparted surface free energy is diminished as a consequence of thermal conductivity toward the interior of the solid. It is therefore necessary to transfer our attention from the atomic and molecular levels to that of the macro level. At this level, controlling the dispersion of heat around the surface of the solid becomes an important issue. After the reaction has commenced, heat energy is dispersed rapidly from isolated active sites, which makes it necessary to concentrate the active sites, that is, achieve a high concentration of precious metals.

### 3.3.3. Scenario (2)

We will go on to look at the effective use of energy in scenario (2), in which the reaction does not proceed. In this scenario, molecules satisfying the conditions for reaction impart some of their energy to surface free energy through collisions, and as a result lose their energy. Figure 4 shows the phenomenon on the solid catalyst surface considered from the macro level; molecules with a translational energy greater than that of  $E_a'$  penetrate the bottom layers of the catalysts without causing a reaction and lose energy by colliding with macro pores. This reduces the number of molecules with energy levels greater than that of  $E_a'$  at the surface

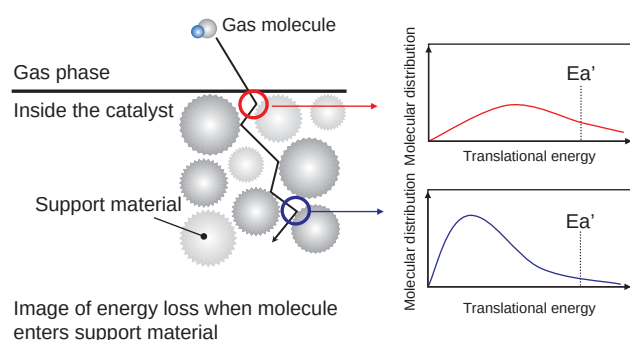


Fig. 4 Conceptual diagram of efficient usage for translational energy

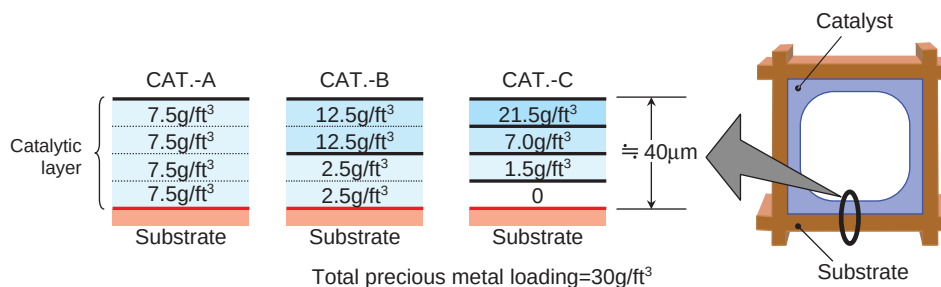


Fig. 5 Pd distribution of test piece

of the catalyst. To prevent this, it is necessary to position the active sites as much as possible at the surface of the catalyst, in close proximity to the gas phase.

### 3.4. Results of Study of Catalyst Modification

The considerations discussed above indicated that the following two methods would be necessary to effectively exploit the energy of molecules to enable them to cross the energy barrier for reaction and cause a reaction to proceed:

- (1) Increasing the concentration of active sites, i.e. increasing the concentration of precious metals
- (2) Ensuring the precious metals in the top layer of the catalyst

Tests were therefore conducted to verify the effectiveness of these methods, and studies were conducted of relevant catalyst specifications.

## 4. Results and Discussion

### 4.1. Catalyst Design

#### 4.1.1. Achievement of high concentration of precious metals in top layer

Lean air-fuel ratios (air in excess of fuel for a stoichiometric air-fuel ratio) are employed to reduce exhaust emissions at engine start, before the catalyst has warmed up. Pd is known to possess excellent HC conversion performance in a lean condition<sup>(8)</sup>. Pd was therefore employed in the top layer of the catalyst developed in this project.

Tests were conducted to study the effect of Pd concentration on light-off performance. Four-layer coat catalysts were manufactured as test pieces using only Pd. Figure 5 shows the structure of these catalysts. A fixed Pd loading was employed in each catalyst, but the concentration in the top layer was varied.

As Fig. 6 shows, light-off performance changes in proportion to the concentration of Pd in the top layer. The test catalyst with the highest concentration of Pd in the top layer displayed the best light-off performance.

These results verified that the concentration of Pd in the top layer contributes significantly to the light-off performance of the catalyst.

In addition, the results showed that the distribution of Pd had no effect on performance at 350 °C and above, when the catalyst is activated.

#### 4.1.2. Reducing the concentration of precious metals in the bottom layers of the catalyst

When the catalyst is activated, changes in driving conditions

(acceleration, deceleration, etc.) tend to increase NO<sub>x</sub> emissions. The use of Pt and Rh, which display excellent NO<sub>x</sub> conversion performance<sup>(9)-(11)</sup>, in the bottom layers of the catalyst developed in this project enabled the achievement of conversion performance identical to that of a conventional catalyst when activated with an 80% reduction in precious metal loading.

#### 4.2. Achievement of a High Concentration of Precious Metals in the Top Layer - Issues and Measures

A catalyst with a high concentration of precious metals in the top layer was manufactured using a standard support material and subjected to a heat resistance test at 900 °C. After the test, the catalyst failed to display the expected light-off performance. The cause of this phenomenon was theorized as follows:

Alumina is employed as the support material for precious metals in automotive catalysts. To increase the probability of the alumina coming into contact with exhaust gas,  $\gamma$  alumina with a high specific surface area is used. However, when alumina is exposed to high temperatures, it undergoes a phase transition in its crystal structure from that of  $\gamma$  phase to  $\alpha$  phase. This reduces the specific surface area, which in turn reduces the distance between the grains of

precious metal and causes sintering. As a result, the number of active sites drops, and light-off performance declines.

To respond to this issue, other metallic elements were added to alumina in an attempt to stabilize its crystalline structure and increase its resistance to high temperatures. The elements formed compounds with part of the alumina, generating a crystal structure that is stable at high temperatures. In addition, the modified alumina and  $\gamma$  alumina share a common layer in their crystal structures that makes it easy for linkages to form; the crystal structure becomes highly stable at the interface, controlling the formation of  $\alpha$  alumina. It was hypothesized that the use of this method would ensure the stability of the crystal structure of the alumina at high temperatures.

Figure 7 shows the crystal structure change in the conventional alumina and the newly developed alumina with an X-ray diffractometer after heat resistance tests at 1 100 °C to verify the effectiveness of this method of stabilizing the crystal structure. The conventional alumina shows numerous  $\alpha$  phase diffraction peaks, indicating a phase transition from that of  $\gamma$  phase to  $\alpha$  phase. By contrast, no  $\alpha$  phase diffraction peaks are shown for the modified alumina, indicating that the phase transition from  $\gamma$  to  $\alpha$  phase has been controlled, thus verifying the effectiveness of adding metallic

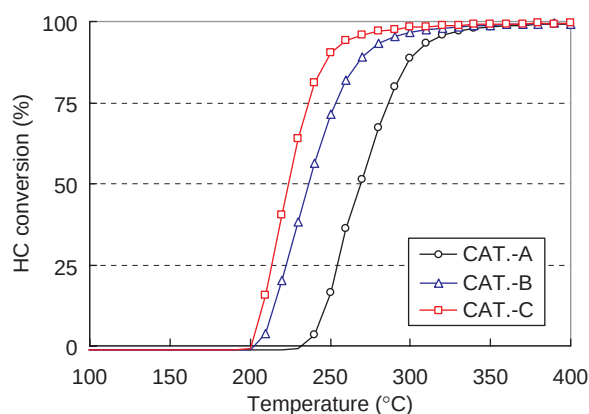


Fig. 6 Relationship between Pd concentration in top layer and HC light-off temperature

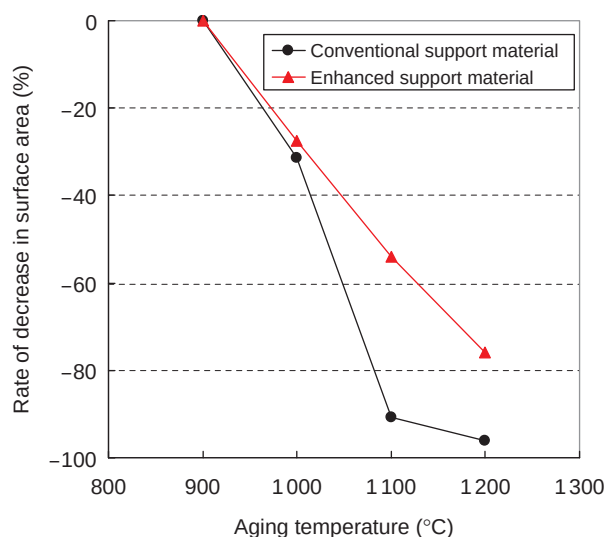


Fig. 8 Effect of enhancing support materials on specific surface area

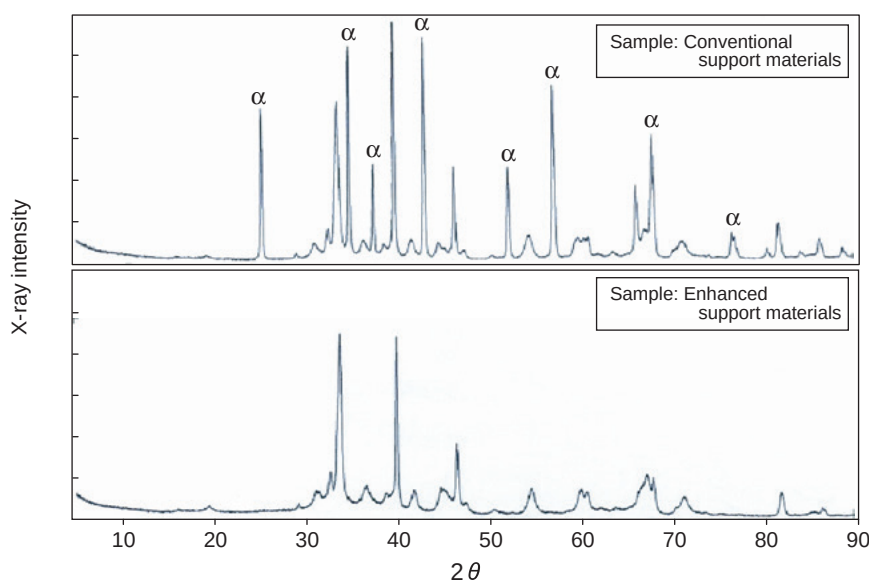


Fig. 7 XRD pattern of support materials (Aging condition:1 100°C)

elements to the alumina as a method of stabilizing the crystalline structure.

Figure 8 shows changes in the specific surface area of conventional alumina and the modified alumina after high-temperature heat resistance tests for a fixed period of time. The specific surface area of the conventional alumina changes rapidly above 1 100 °C, and declines by approximately 60% between 1 000 °C and 1 100 °C. By contrast, the specific surface area of the modified alumina is reduced by only approximately 25% between 1 000 °C and 1 100 °C, and the change above 1 100 °C is slower than that displayed by the conventional alumina. These results indicate that the reduction in specific surface area has been effectively controlled by modification of the alumina.

To verify the effectiveness of the modified alumina in controlling the sintering of Pd, catalysts were manufactured using identical amounts of Pd to support conventional and modified alumina, and subjected to heat resistance tests at 1 100 °C. Figure 9 shows the results of Transmission Electron Microscopy (TEM) of the Pd grains in these catalysts. In the catalyst employing conventional alumina, the diameter of the Pd grains varies between 30 and 300 nm, and sintering has occurred. In the catalyst employing the modified alumina, the diameter of the Pd grains is approximately 20 nm, the grains are evenly dispersed, and no sintering has occurred.

#### 4.3. Effect of Top Layer Pd Concentration on Heat Resistance

Catalysts with top layer Pd concentrations of 12% (12%-Pd) and 18% (18%-Pd) were manufactured and subjected to heat resistance tests from 900 °C to 1 100 °C, after which light-off performance was tested in model gas tests. As Fig. 10 shows, the 18%-Pd catalyst displayed superior light-off performance to that

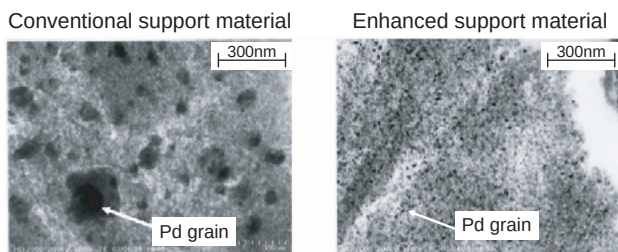


Fig. 9 TEM image of Pd grain (Aging condition: 1 000°C)

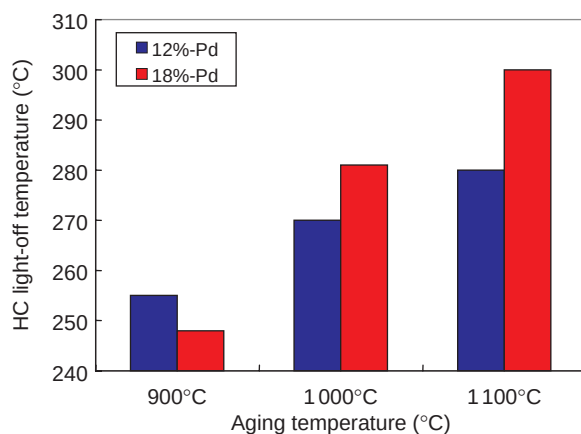


Fig. 10 Relationship between Pd concentration and HC light-off temperature

of the 12%-Pd catalyst after heat resistance testing at 900 °C. However, the effect was reversed with change in temperature, with the 12%-Pd catalyst displaying superior light-off performance after testing at temperatures of 1 000 °C and above. The catalyst with the higher concentration of Pd showed a significantly greater decline in HC light-off performance at 1 000 °C than that of the other catalyst; the light-off temperatures of the 12%-Pd and 18%-Pd catalysts increased by 15 and 33 °C respectively, between 900 and 1 000 °C. This is believed to be because the 1.5 times greater concentration of Pd in the 18%-Pd catalyst brings the grains into closer proximity, and sintering therefore occurs despite the use of the modified alumina as a support material.

These results indicate that optimal Pd concentration exists with respect to the temperature of the exhaust gas in the vehicles in which the catalyst will be employed.

#### 4.4. Comparison of the PZEV Mass-production Catalyst and the Modified Catalyst

Based on the test results discussed above, a catalyst with half the precious metal loading of the PZEV mass-production catalyst was manufactured. Figure 11 shows the results of tests comparing the PZEV and the newly developed catalyst. The newly developed catalyst displays identical HC light-off performance and conversion performance after warm-up to the PZEV catalyst.

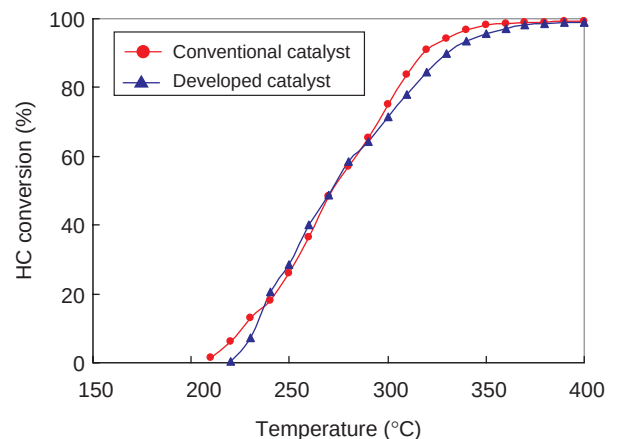


Fig. 11 Comparison of HC light-off temperature in conventional catalyst and developed catalyst

## 5. Conclusion

Major conclusions of the research discussed above are as follows:

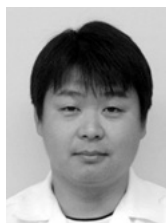
- (1) Consideration of the catalyst reaction mechanism indicated that the concentration of precious metals in the top layer was an important factor in the achievement of enhanced light-off performance, and this hypothesis has been verified experimentally.
- (2) Increasing the concentration of precious metals in the top layer and reducing its thickness, at the same time reducing the concentration of precious metals in the bottom layers, has enabled a reduction in the amount of precious metals employed in each catalyst.
- (3) Sintering of the precious metals in the catalyst was controlled by increasing the concentration of precious metals and employing a high heat resistance support material.
- (4) Appropriate concentrations of precious metals exist for different temperatures to which the catalysts will be exposed.

This project succeeded in developing a catalyst with a reduced precious metal loading that displays identical performance to that of a conventional catalyst. The newly developed catalyst is being studied for use as a mass production catalyst for 2006 models.

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## ■ Authors ■



Syouji INOSE



Tatsuya OKAYAMA