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Research Report

Alumina-Ceria-Zirconia Composite Oxide for Three-Way Catalyst

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三元触媒用アルミナ-セリア-ジルコニア複合酸化物

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Abstract

Further purge performance improvement of the three-way catalyst is necessary because of the atmosphere environment preservation. In this report, for heat-resistance improvement of the CeO_2-ZrO_2 solid solution (CZ) which was equipped with oxygen storage capacity (OSC), we proposed new catalyst promoter "ACZ".

ACZ consists of CeO_2-ZrO_2 solid solution (CZ) particle with the diffusion barrier layer and the nanometer size, which was made with alumina (A).

The CZ crystallite size after durability test of the catalyst which contains ACZ was small compared with the usual catalyst and the sintering of the platinum loaded on the catalyst, was also restrained.

As a result, as for the catalyst which contains ACZ, the oxygen storage capacity and the catalyst activation temperature improved substantially compared with the usual catalyst.

Keywords Catalyst, Durability , Environment , Gasoline engine, Aluminum oxide, Ceria, Zirconia

要　旨

大気環境保全のため三元触媒の更なる浄化性能向上が必要である。

この報告では，酸素貯蔵能 (OSC) を備えたCeO_2-ZrO_2固溶体 (CZ) の耐熱性向上を目的とし，新しい助触媒"ACZ"を提案した。

ACZは，アルミナ (A) で作られた拡散障壁層とナノメートルサイズのCeO_2-ZrO_2固溶体 (CZ) 粒子から成るものである。

ACZを含む触媒の耐久試験後のCZ結晶子径は，従来触媒に比べて小さく，触媒上の白金の焼結も抑制された。その結果，ACZを含む触媒は従来触媒に比べて酸素貯蔵量と触媒活性化温度が大幅に向上した。

キーワード　触媒，耐久性，環境，ガソリンエンジン，アルミニウム酸化物，セリア，ジルコニア

1. Introduction

Concerns regarding environmental protection are increasing, and the demand for improvements in clean exhaust and fuel for automobiles is increasing each year all over the world. For example, California is now dealing with the LEV (low emission vehicle) II standards, which are the strictest standards yet seen and require significant decreases in hydrocarbon (HC) and nitrogen oxide (NOx) emissions in exhaust gases.

Reductions in HC and NOx gas emitted from current gasoline engines is being achieved primarily by improvements in catalysts, and by improvements in either the engines themselves or methods for controlling them.

However, approximately 70% of HCs exhausted in running mode (LA#4), shown in **Fig. 1**, are emitted during the approximately 100 second period beginning with engine start-up when the catalyst is cold and being activated. Consequently, early activation of catalyst during the cold period is an important consideration in reducing HC emission.

On the other hand, NOx is emitted over the entire mode. Consequently, in addition to cold-period activation of the catalyst, improvement in cleaning performance after warm-up is also an important consideration in NOx reduction.[1)]

Three-way catalysts for automobiles have characteristics whereby HC, CO and NOx are cleaned with good efficiency in the vicinity of theoretical air/fuel ratios. However, air/fuel ratios for automobiles vary greatly with time depending on operating conditions. The NOx exhaust behavior in the LA#4 running mode is presented in detail (**Fig. 2**). A large volume of NOx exhaust is produced during acceleration when the air/fuel ratio (A/F) varies greatly, because the cleaning efficiency of the catalyst decreases at ratios that fall outside the theoretical air/fuel ratio. Consequently, a catalyst is desired that has high NOx cleaning performance, even when the A/F ratio varies greatly.

With current three-way catalysts, the addition of auxiliary catalyst having oxygen storage capacity (OSC) mitigates A/F variation and adjusts the atmosphere at the surface of the catalyst to nearly theoretical air/fuel ratios, thereby controlling NOx discharge.

Ceria is commonly used as the primary component of oxygen storage materials (OSC materials). Thus, a method that has been proposed and implemented as a measure for improving the oxygen storage/release capacity (OSC) involves production of a solid solution by introducing an element having a smaller ionic diameter than Ce ions, such as Zr or Y, into the ceria. By doing so, the space surrounding the oxygen is increased, thereby facilitating reversible storage and release of oxygen in the matrix.[2, 3)] In addition, it has been reported that increases in OSC have been achieved by forming ceria-zirconia solid solutions (CZ).[4)] However, conditions of catalyst use are becoming increasingly extreme, and catalysts used in automobiles now require a high heat resistance of approximately 1000°C. As such, CZ has been investigated in regard to changes of state that occur during heat resistance testing, and a dramatic decrease in

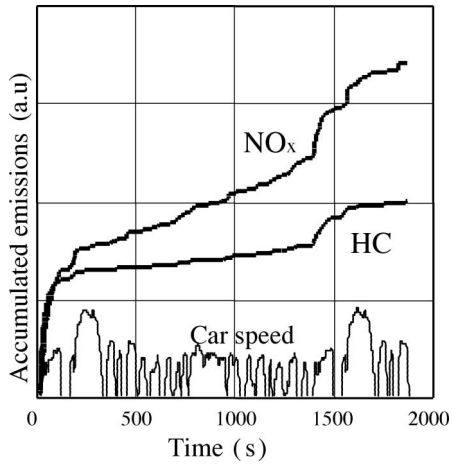

Fig. 1 HC, NOx emissions (LA#4).

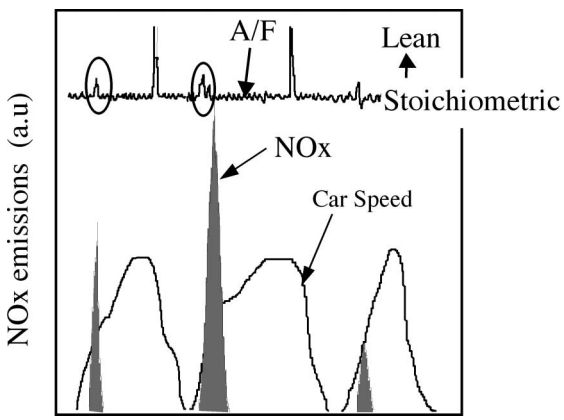

Fig. 2 Transition of NOx, A/F(LA#4).

specific surface area to a few square meters per gram or less has been determined to occur at temperatures of 1000°C or greater with increasing coarseness of the CZ crystallites. A dramatic reduction in the size of oxygen entrance and exit openings thus occurs in the oxygen storage material, leading to a decrease in OSC.

The objective of our research has been (1) to offer concepts for improving heat resistance and performance of auxiliary catalysts, and (2) to develop a novel oxygen storage material based on these concepts.

2. Methods

2. 1 Diffusion barrier concept

The concept of improving the heat resistance of ceria-zirconia solid solution (CZ) is described in **Fig. 3**. As indicated in the top profile of Fig. 3, particle growth occurs due to thermal degradation when CZ is subjected to heat-resistance testing.

As a result, the specific surface area of the CZ decreases, causing a reduction in OSC. With the objective of controlling particle growth, suppression of CZ particle growth by providing a stable substance having a size on the order of nanometers between the CeO_2-ZrO_2 solid solution (CZ) particles was envisioned. Al_2O_3 was thus selected as the particle growth inhibitor due to its resistance to reaction with CZ and its high heat resistance. Thus, the heat resistance of oxygen storage materials (OSC materials) was increased based on this diffusion barrier concept. Alumina-ceria-zirconia composite oxide produced based on the diffusion barrier concept by complexing CZ with alumina (A) having a size on the order of nanometers is referred to as "ACZ".[1, 5 - 7)]

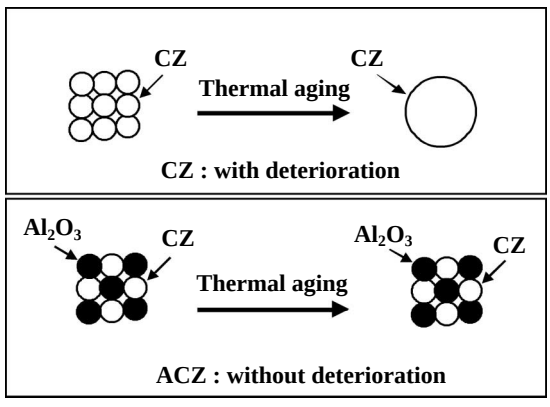

Fig. 3 New diffusion barrier concept.

2. 2 Preparation method for ACZ powder, CZ powder and catalyst containing the same

ACZ powder and CZ powder were synthesized by a sol-gel method and a coprecipitation method. Commercially-available activated alumina powder of 50 wt% and a small amount of binder component were added to the synthesized ACZ powder to produce a solid solution, which was wash-coated onto a 400 cpsi ceramic monolithic honeycomb, followed by sintering for 1 h at 500°C. Platinum nitrate aqueous solution and rhodium nitrate aqueous solution were then used to support the noble metals, thus producing a monolithic catalyst. In addition, a monolithic catalyst containing CZ powder was produced as a comparative catalyst, in which CZ powder was synthesized under the same conditions as the ACZ powder, with the exception that alumina raw material was not added. The two catalysts had equivalent component weights, and so a commercially-available active alumina powder was added to the catalyst containing CZ powder in an amount equivalent to that contained in the ACZ powder. The catalysts were subjected to the same wash-coat process in the same amounts to prepare monolithic catalysts.

2. 3 Determination of ACZ fine structure

ACZ powder and CZ powder were subjected to heat resistance testing for 5 h at 1000°C, and in order to investigate CZ particle size and compositional element uniformity, energy dispersion x-ray spectroscopy (EDX) and SEM observation were performed. With regard to EDX analysis and SEM observation, the powder was enclosed in resin, and the powder cross-section was then polished to a mirror surface. The micron-order uniformity of the compositional elements on the polished surface was investigated by EDX analysis. The compositional element uniformity and CZ particle diameter were investigated on the nanometer order using a reflected electron image for SEM observation.

In addition, the catalyst slurry used for wash-coating produced as described in **Section 2. 2** was subjected to heat resistance testing for 5 h at 1000°C in open air, and XRD was then performed. XRD measurements were used to determine CZ crystallite diameter via the Scherer Formula.

2. 4 Measurement of specific surface area

The synthesized ACZ powder and CZ powder were subjected to heat resistance testing for 10 h at 900-1200°C in open air, and the specific surface area was measured by nitrogen absorption (BET method).

2. 5 Measurement of OSC using a model gas

The method for measuring oxygen storage capacity (OSC) using a model gas is shown in **Fig. 4**. Nitrogen balance gas containing 1 vol% hydrogen and nitrogen balance gas containing 1 vol% of oxygen were alternately passed through a catalyst, and the amount of oxygen stored on the catalyst and the amount of oxygen released from the catalyst were measured in the production of H_2O by a reaction between gas phase hydrogen and stored oxygen. The catalyst used in measurement was a material produced by subjecting palletized catalyst supporting 1 wt% Pt to a heat resistance test for 10 h at 1000°C. Measurement was performed under temperature conditions of 300°C, 500°C and 700°C, respectively.

2. 6 Catalyst evaluation

Two types of catalysts prepared by the method described in **Section 2. 2** were attached to the exhaust pipe of an automobile, and durability testing was performed for 100 h at a catalyst bed temperature of 950°C. Analysis was performed by XRD, and by measurement of the exhausted amount of nitrogen oxide in the actual engine exhaust.

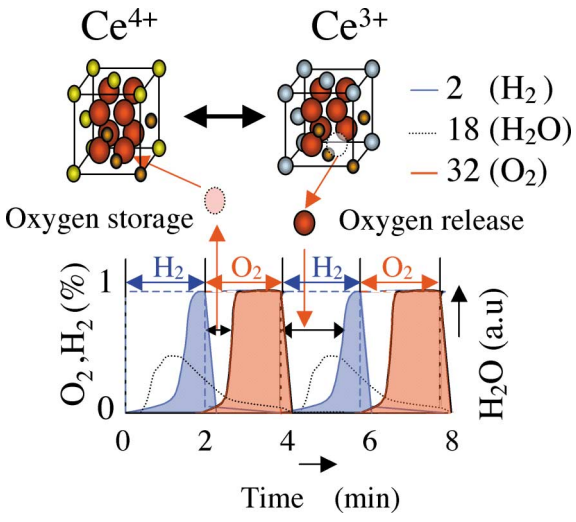

Fig. 4 OSC measurement method.

3. Results

3. 1 ACZ fine structure

A broad range of samples was subjected to EDX analysis in order to locally analyze a number of regions on the micrometer order. As a result, it was determined that the Ce/(Al + Ce + Zr) x-ray intensity ratio and the Zr/(Al + Ce + Zr) x-ray intensity ratio were constant. It was thus confirmed that the ACZ powder had a uniform constitutional element distribution on the micrometer order, even when subjected to a heat-resistance test for 10 h at 1000°C. The results of SEM observation are presented in **Fig. 5**.

The photograph in Fig. 5 is a reflected electron image, and the regions that appear dark represent light material (alumina), whereas the regions that appear light represent heavy material (CZ). From Fig. 5, the ACZ was determined to be a solid solution composed of approximately 10 nm CeO_2-ZrO_2 grains dispersed in alumina, and complex oxide on the nanometer order was confirmed to be formed as intended according to the concept of the diffusion barrier.

Figure 6 presents the XRD profile after subjecting catalyst slurries to heat-resistance testing for 5 h at 1000°C. The results of quantitative analysis show that with CZ powder and ACZ powder, the ceria contained in the powder is contained as a uniform CeO_2-ZrO_2 solid solution. The particle diameter of the ACZ powder in the CeO_2-ZrO_2 solid solution was determined to be 4.6 nm, and the particle diameter of the CZ powder was 6.2 nm. It was thus confirmed that sintering of the CZ in the ACZ was suppressed.

3. 2 ACZ specific surface area and OSC

ACZ and CZ were subjected to specific surface

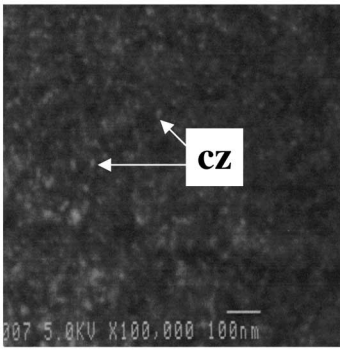

Fig. 5 Sectional structure of ACZ.

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area measurement subsequent to heat-resistance testing for 10 h in open air at 900-1200°C, and the results are presented in **Fig. 7**. ACZ was found to maintain high specific surface area relative to CZ, even at high temperature. The results of OSC measurements are presented in **Fig. 8**. The ACZ-containing catalyst was confirmed to have dramatically improved OSC relative to the CZ-containing catalyst.

3. 3 Maintenance of performance and condition of the catalyst containing ACZ

The catalysts were subjected to durability testing in actual engine exhaust for 100 h at an inlet gas temperature of 950°C, and the cleaning capacity of the two catalysts containing ACZ and CZ were compared. The results, as shown in **Fig. 9**, indicate that catalyst containing ACZ produced an NOx exhaust amount in mode testing that was 20% less than that of the CZ-containing catalyst, and thus that the intended improvement in performance was obtained by using ACZ. The catalyst layer of this catalyst was also observed by XRD, and the results of quantitative analysis indicate that in both cases, ceria was present as CeO_2-ZrO_2 solid solution. The particle diameter of the ACZ powder in the CeO_2-ZrO_2 solid solution was 8.7 nm, and the particle diameter of the CZ powder was 17.2 nm. The thermal coagulation inhibitory effect with respect to the CZ in the ACZ was confirmed after durability testing using actual exhaust (**Table 1**). Moreover, as shown in Table 1, catalyst that employed ACZ was found to exhibit a capacity for inhibiting Pt sintering.

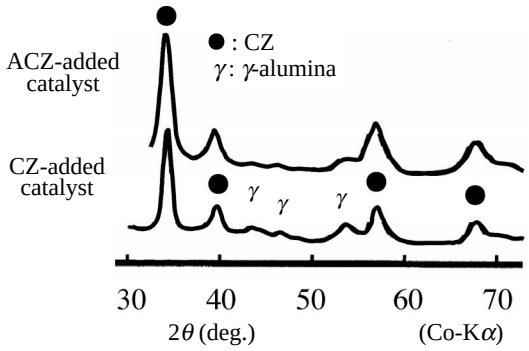

Fig. 6 XRD profile after 5h durability test in air at 1000°C.

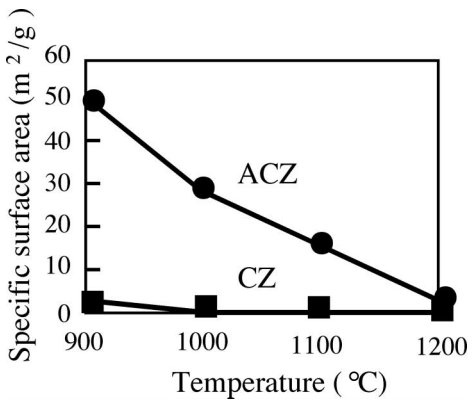

Fig. 7 Surface area after 10h durability test in air.

4. Conclusions

A diffusion barrier concept was proposed in conjunction with the existing concept of CZ solid solution formation for improving heat resistance and increasing performance in auxiliary catalysts. An

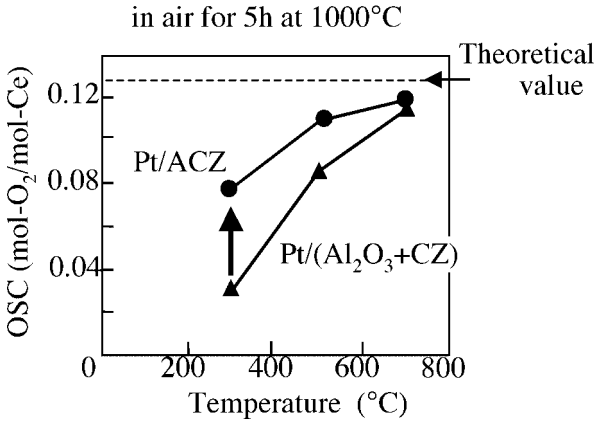

Fig. 8 OSC (after durability test).

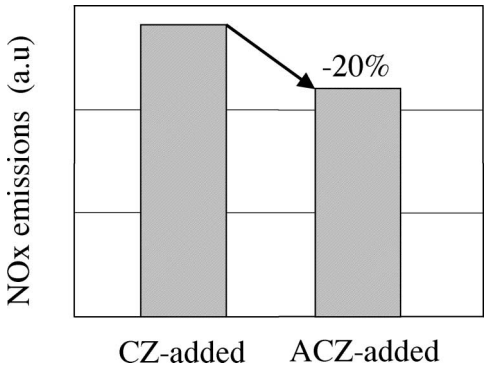

Fig. 9 NOx emissions.

Table 1 Particle diameters of Pt and CZ after durability test at 950°C.

	ACZ-added catalyst	CZ-added catalyst
Pt particles	19.6nm	23.7nm
CZ particles	8.7nm	17.2nm

alumina-ceria-zirconia complex oxide (ACZ) was developed based on the above-described diffusion barrier concept, and this material was determined to be capable of improving OSC after heat resistance testing. It was confirmed that the use of this auxiliary catalyst allows improvement in catalyst metal heat resistance and catalytic performance.

Acknowledgements

The authors would like to thank to the various individuals who were involved in the preparation, aging, analysis, and evaluation of the catalysts.

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(Report received on Sep. 29, 2002)

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