Improvement of OSC performance for CeZrO$_4$ solid solution with Al$_2$O$_3$ diffusion barrier

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Az OSC (oxigéntároló képesség) teljesítménynövelése Al$_2$O$_3$ diffúziógátat tartalmazó CeZrO$_4$ szilárd oldatban

Annak érdekében, hogy a CeO$_2$-ZrO$_2$ szilárd oldata (CeZrO$_4$) még inkább felhasználható legyen az autóipari kipufogógáz-katalizátorok oxigéntároló anyagaként, kidolgoztunk egy Al$_2$O$_3$ és CeZrO$_4$ vegyületekből álló, nanométer finomságú kompozit anyagot (az ACZ-t). Az oxigéntároló képesség (OSC) további javítása céljából a szerzők szisztematikus kutatást végeztek, amely kimutatta, hogy a többlet Al$_2$O$_3$ adagolás nemcsak a CeZrO$_4$ termikus stabilitását növeli, hanem annak oxigéntároló képességét, különösen pedig az oxigén leadását (OSC-r) is. E vizsgálatok során a redukáló kezelés révén jelentősen javult az ACZ teljes OSC-je (az OSC-c). A redukált ACZ OSC-c mutatószáma az 1000 °C hőmérsékleten végzett kezelés után érte el elméleti maximumát.

Kulcsszavak: Al$_2$O$_3$, CeO$_2$, ZrO$_2$, oxigéntároló képesség, háromutas katalizátor

Keywords: Al$_2$O$_3$, CeO$_2$, ZrO$_2$, oxygen storage capacity, 3-way catalyst

1. Introduction

CeZrO$_4$ as the oxygen storage material has been indispensable component for three-way catalysts of gasoline automobiles because it plays a role to maintain the air/fuel (A/F) ratio of the exhaust gas around 14.6 in the catalyst [1]. CeZrO$_4$ has been improved on the durability and the OSC performance since 1988 to develop each generation of advanced three-way catalysts to fit that of regulations [2–5]. The latest oxygen storage material, ACZ, has a novel microstructure, which consists of Al$_2$O$_3$ and CeZrO$_4$ mutually intervening in nanometer scale. In ACZ, Al$_2$O$_3$ has a role of a diffusion barrier to inhibit the sintering of CeZrO$_4$ crystallites [6]. The Al$_2$O$_3$ diffusion barrier is effective in practical use; however, systematic studies for basic property of ACZ are not enough. This study was conducted to clarify the effect of the additional Al$_2$O$_3$ into the CeZrO$_4$ on its physical properties and the OSC characteristics and to improve the performance further more.
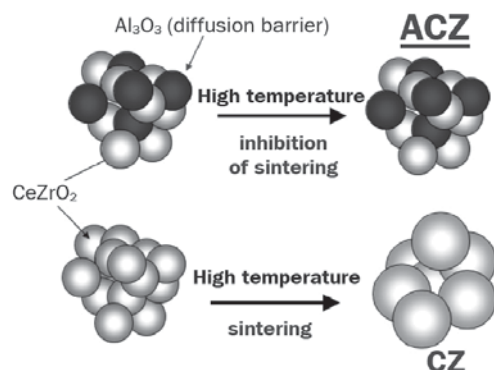

Fig. 1. A schematic figure of sintering inhibition by the Al$_2$O$_3$ introduction into CeZrO$_4$ as a diffusion barrier

1. ábra Al$_2$O$_3$ diffúziógátló anyag által a CeZrO$_4$-ben okozott zsugorodásgátlás vázlatos ábrázolása

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was born in 1970 in Japan. He has been involved in the development of 3-way catalysts for gasoline automobiles in Catalyst Lab. of Toyota Central R&D Labs., Inc. since he finished his master's course in Nagoya University in 1995. He also has attended to a doctoral course in Nagoya University since 2006 as an adult graduate student. Recent research targets are the development of oxygen storage materials represented by CeO$_2$, the elaboration of novel catalytic supports, and the design new catalytic active species.

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2. Experimental

2.1. Preparation of catalysts

ACZ was used as a catalytic support and also an oxygen storage material. This composite oxide was prepared by co-precipitation process of nitrate and following the calcination at 700 °C [7], which had a composition of 1/1/1 molecular ratio of Al$_2$O$_3$/CeO$_2$/ZrO$_2$. The CeZrO$_4$ solid solution without Al$_2$O$_3$ was used as a comparative material, which is abbreviated as CZ. CZ was prepared by the same process as ACZ and had a composition of 1/1 molecular ratio of CeO$_2$/ZrO$_2$. The durability test was conducted on the ACZ and CZ from 800 and 1000 °C for 5 h in air. Moreover, the effect of reductive treatments was estimated at four levels of temperature on the ACZ to improve its OSC (Table 1). Prior to evaluating OSC performance, 2 wt% Pt were loaded on the ACZ and CZ supports with using impregnation of Pt(NO$_2$)$_2$(NH$_3$)$_2$ in diluted nitric acid solution.

Catalysts	Atmosphere for heat treatment	Temperature °C	Pt loading wt%	SSA m²/g
ACZ	Air	700	2	103
ACZ-H2-700	H₂(5%)/N₂	700	2	97
ACZ-H2-800	↑	800	2	76
ACZ-H2-900	↑	900	2	45
ACZ-H2-1000	↑	1000	2	32
CZ	Air	700	2	54

Table 1. Prepared catalysts by the reductive treatment
1. táblázat Redukáló kezeléssel előállított katalizátorok

2.2. Characterization of catalyst

BET specific surface areas of ACZ and CZ before and after durability testing were measured by the BET one-point method using the automatic surface area analyzer (model-4232II, Micro-Data). Diffraction patterns of catalysts were measured at diffraction angles (2-theta) from 10 to 80° using X-ray diffraction apparatus (RINT-TTR, Rigaku) at 50kV, 300mA.

2.3. Evaluation of catalytic performance

Generally, OSC is categorized as two types. The one is an oxygen storage capacity complete (OSC-c) that shows saturated oxygen storage and release amount, and the other is an oxygen release rate (OSC-r) that indicates oxygen initial release rate. The former was measured by a thermogravimetric analyzer (TGA-50, Okurariken). After pretreated at 500 °C for 15 min under an O_2 (20%)/N_2 (balance) atmosphere, Pt loaded catalyst was cooled to 300 °C in the same oxidative atmosphere. When the temperature reached the predetermined temperature, the atmosphere was switched from O_2 (20%)/N_2 to H_2 (20%)/N_2 until the weight decrease of the catalyst was no longer detected. Subsequently, the atmosphere was changed back to O_2 (20%)/N_2, and the atmosphere and temperature were maintained until the weight increase in the catalyst was no longer detected. These steps were repeated until the weight reduction under H_2 (20%)/N_2 and weight increase under O_2 (20%)/N_2 became almost equal. Subsequently, additional two cycles were repeated, followed by calculation of the average of each weight reduction and increase. The saturated OSC, OSC-c, was denoted as the amount of O_2 adsorption/desorption per mole of CeO_2 included in the catalyst (O_2-mol·CeO_2-mol^{-1}). The later was derived by evaluating the amount of CO_2 formation under an alternative atmosphere, where CO (2%)/N_2 and O_2 (1%)/N_2 were introduced into a catalyst every 3 min, using a fixed-bed flow reaction apparatus (CATA5000-4, Best SOKKI). 1 g of a catalyst was filled in a quartz reaction tube with a diameter of 15 mm, and each reaction gas was introduced into the reaction tube with the flow rate of 7 L/min at the determined temperature. In this measurement, the gradient of the tangential line to the CO_2 production curve was the amount of oxygen released per second. CO and CO_2 were analyzed by a non-dispersive infrared (ND-IR) type analyzer and O_2 was quantified with a magnetic oxygen analyzer. [7].

3. Results and discussion

The BET specific surface area (SSA) of ACZ was twice as large as that of CZ at 700 °C (initial condition). In addition, ACZ maintained a higher SSA than CZ after each durability test; for example, after the heat treatment at 1000 °C, ACZ kept 20 m²/g but that of CZ fell down below 1 m²/g (Fig. 2). The crystallite of $CeZrO_4$ in ACZ at 700 °C (initial condition) by XRD had a size of about 6 nm, and sintered at most up to about 10 nm at 1000 °C. On the other hand, the crystallite size of $CeZrO_4$ in CZ after durability test at 1000 °C reached 20 nm. $CeZrO_4$ in CZ sintered twice as large as that in ACZ, although the initial sizes of their $CeZrO_4$ were almost the same as 8 or 6 nm (Fig. 3). These results indicate that the addition of Al_2O_3 not only keeps a higher SSA, but also suppresses the crystallite growth of $CeZrO_4$, which means the Al_2O_3 addition enhances the heat resistance of $CeZrO_4$ in ACZ.
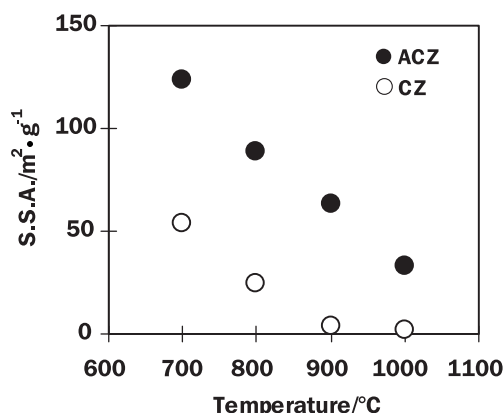

Fig. 2. BET SSA as a function of temperature
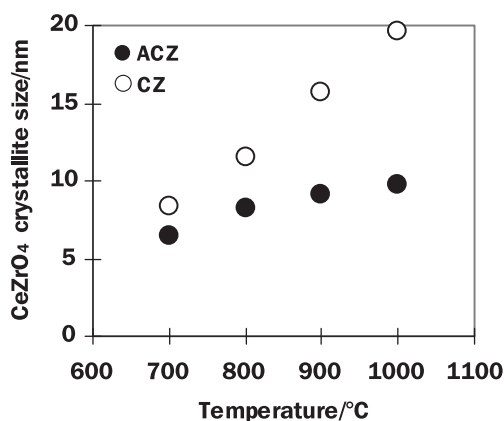*2. ábra A BET SSA változása a hőmérséklet függvényében*

Fig. 3. CeZrO₄ crystallite size as a function of temperature
3. ábra A CeZrO₄ krisztallit mérete a hőmérséklet függvényében

The OSC-c of the Pt loaded ACZ catalyst measured at 100 or 300 °C was slightly bigger than that of the corresponding CZ catalyst and that of ACZ at 500 °C much bigger than that of the CZ catalyst (Fig. 4). On the other hand, the OSC-r of the ACZ catalyst at each temperature from 100 to 300 °C was better than those of CZ. In particular, the OSC-r of ACZ measured at

300 °C was about 1.5 times faster than that of the CZ catalyst (Fig. 5). The $CeZrO_4$ crystallite sizes in these two catalysts were almost identical (see results at 700 °C in Fig. 3) and the Pt particle size in the ACZ catalyst (0,7 nm), which was measured by low temperature CO adsorption technique [7]. The value was about one-half of the Pt particle size in CZ (1,2 nm); in other words, the numbers of activation sites for the oxygen release in ACZ were twice as much as that in CZ. This means that the finer Pt particles in ACZ promote the OSC-r more than the coarser ones in CZ. The OSC-enhancement mechanism is thought to be come from larger number of activation sites and/or closer distance between each activation sites in ACZ. These results also suggest that the introduction of the Al_2O_3 diffusion barrier into $CeZrO_4$ is effective to promote the OSC performance, particularly the OSC-r.
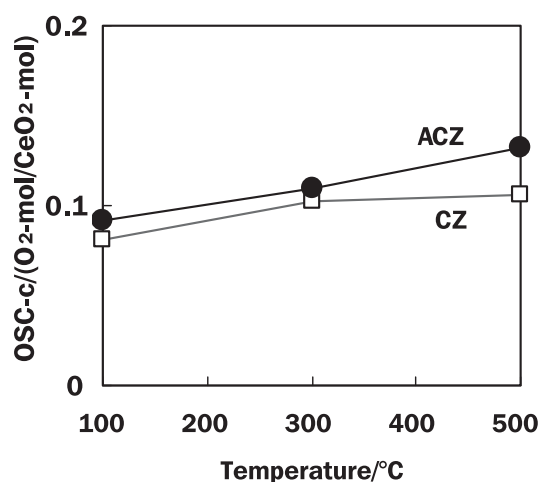

Fig. 4.   OSC-c of fresh catalysts. Circle: ACZ, square: CZ
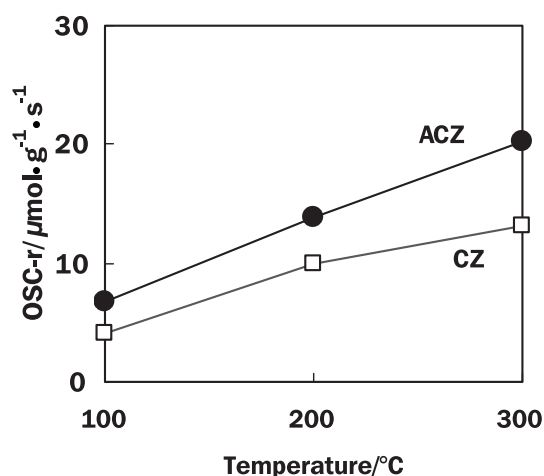*4. ábra   A friss katalizátorok OSC-c mutatószáma. Kör: ACZ, négyzet: CZ*

Fig. 5.   OSC-r of fresh catalysts. Circle: AZ, square CZ.
5. ábra   A friss katalizátorok OSC-r mutatószáma. Kör: ACZ, négyzet: CZ

For further improvement of the OSC-c and the OSC-r, ACZ was observed in the samples reduced in an atmosphere composed of H_2 (5%) and N_2 (balance) from 700 to 1000 °C prior to Pt loading. The OSC-c of ACZ, which were measured at 300 °C, increased with the reduction temperatures, and reached to the theoretical maximum after the reduction at 1000 °C (ACZ-H2-1000 in Fig. 6). The XRD pattern of ACZ

reduced at 1000 °C indicated the characteristic peaks of the κ-phase $CeZrO_4$ (Fig. 7), which has regularly-arranged Ce and Zr cations and slightly disordered oxygen [8]. Masui et al. reported the OSC performance of the $CeZrO_4$ with the κ-phase was larger than that of the conventional $CeZrO_4$ [9]; hence the increase of the OSC-c of ACZ-H2-1000 up to the theoretical maximum could be attributed to the formation of this phase.
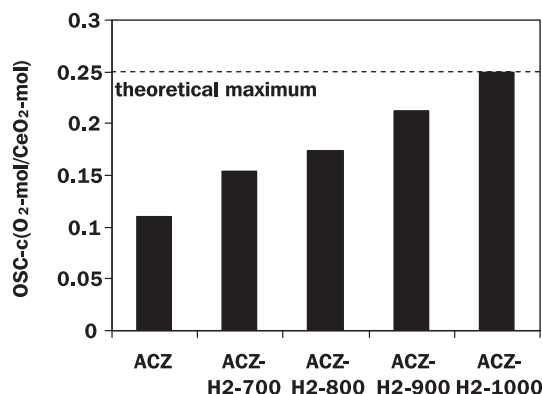

Fig. 6.   OSC-c of reduced catalysts prior to Pt loading was measured at 300 °C
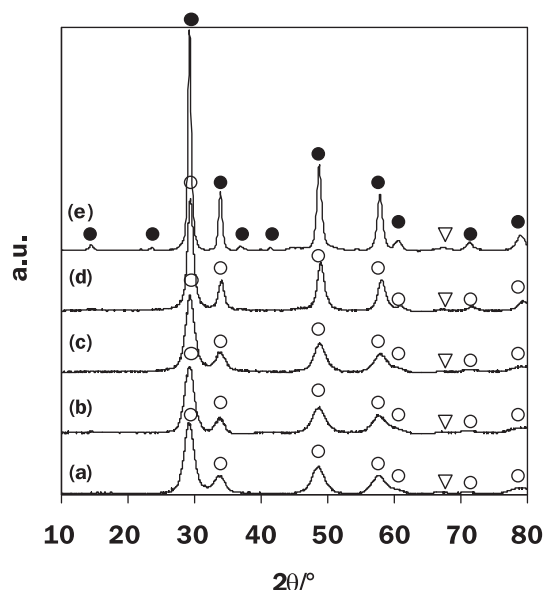*6. ábra   A redukált katalizátorok OSC-c mutatószáma 300 °C hőmérsékleten mérve, a Pt terhelés előtt*

Fig.7.   XRD profile of reduced ACZ (a) as received (fresh); (b) at 700 °C; (c) at 800 °C; (d) at 900 °C; (e) at 1000 °C.
●: κ-phase of $CeZrO_4$, ○: t"-phase of $CeZrO_4$, ▼: γ-Al_2O_3.
7. ábra   A redukált ACZ XRD görbéje: (a) eredeti (friss) állapotban, (b) 700 °C, (c) 800 °C, (d) 900 °C, és (e) 1000 °C hőmérsékleten.
●: a $CeZrO_4$ κ-fázisa; ○: a $CeZrO_4$ t"-fázisa, ▼: γ-Al_2O_3.

In contrast to the OSC-c, the order of the OSC-r varied with the evaluation temperature. The OSC-r of the ACZ catalyst measured at 300 °C increased with the reduction temperature (Fig. 8a), while the OSC-r at 200 °C showed the peak at the reduction temperature of 800 °C (ACZ-H2-800 in Fig. 8b). The oxygen releasing processes are generally considered to consist of the following two main steps; the first one is oxygen volume diffusion inside the lattice, the second one is oxygen transfer on the surface of the $CeZrO_4$ particles [10, 11]. If the crystallite size of $CeZrO_4$ is large enough and the measurement

temperature for the OSC-r is high enough, the volume diffusion rate has a larger influence on OSC-r than the surface diffusion rate [10, 11]. The measurement temperature of 300 °C could be high enough and the bulk diffusion of oxygen could control the OSC-r, therefore the ACZ catalysts, which were reduced at higher temperature and whose κ-phase component ratio were higher, indicates the higher OSC-r with reduction temperature. In contrast, the measurement temperature of 200 °C could be not high enough for diffusion control of bulk oxygen, and oxygen transfer rate on the surface could control the OSC-r measured at 200 °C. Hence, the lacking of the surface and surface-neighborhood oxygen makes the ACZ catalyst reduced at 1000 °C indicate the lowest OSC-r because of the degradation of SSA (32 m^2/g, Table 1.). The ACZ catalyst without reductive treatment, which showed the second lowest OSC-r, could have the small amount of the complete releasable oxygen in $CeZrO_4$ lattice due to dismissing the reductive treatment in spite of maintaining the sufficiently high SSA (103 m^2/g, Table 1.).
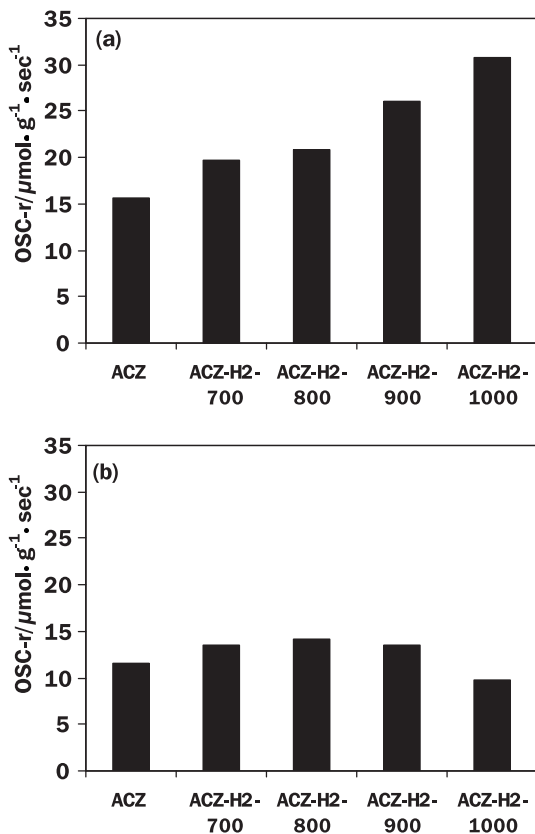

Fig. 8.   OSC-r of reduced catalysts prior to Pt loading were measured at (a) 300 °C; (b) 200 °C

8. ábra   A redukált katalizátorok OSC-r mutatószáma (a) 300 °C, illetve (b) 200 °C hőmérsékleten mérve, a Pt terhelés előtt

According to above discussion, the OSC-r depends on the balance between the increase of the complete releasable oxygen amount in the $CeZrO_4$ lattice (OSC-c), and the keeping of the surface or surface-neighborhood oxygen with SSA after the H_2 reduction.

4. Conclusion

ACZ has more excellent heat-resistance and better OSC-property, particularly OSC-r, than those of conventional CZ. The great progress achieved as a result of inhibition of $CeZrO_4$ crystallite growth by the introduction of Al_2O_3 in nanometer scale. Furthermore, reductive treatments prior to Pt loading at temperatures from 700 to 1000 °C achieved large improvement in the complete oxygen storage capacity (OSC-c). ACZ reduction of 1000 °C prior to Pt loading (ACZ-H2-1000), in particular, indicated the theoretical maximum OSC-c, while maintaining a sufficient SSA. This high-performance OSC-c is derived from the formation of the κ-phase of the $CeZrO_4$ crystallite, where Ce and Zr ions arrange regularly. On the other hand, reductive treatments below 900 °C did not form the κ-phase of the $CeZrO_4$ crystallite in ACZ.

The reductive treatment also improved the oxygen release rate (OSC-r) of the ACZ catalyst; however, its variation against the evaluation temperature and the reduction temperature differed from that of OSC-c. The OSC-r of ACZ catalysts measured at 200 °C showed a maximum value against the reduction temperature at 800 °C, whereas that at 300 °C increased with the reduction temperature, as in the case of OSC-c. The variation of the measured OSC-r depends on the balance between the increase of the complete releasable oxygen amount in the $CeZrO_4$ crystallite lattice, and the keeping of surface or surface-neighborhood oxygen with SSA after the H_2 reduction. Therefore, reduction temperatures should be chosen according to the practical conditions in a three-way catalyst.

Acknowledgment

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