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# Preparation of ceria–zirconia sub-catalysts for automotive exhaust cleaning

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## Abstract

This paper focuses on the development of ceria–zirconia materials which have high thermal stability and high catalytic activity. The $CeO_2$–$ZrO_2$ system is very important as a sub-catalyst in the autoexhaust catalytic converters, especially on the oxygen-storage capacity (OSC). The role of the $CeO_2$–$ZrO_2$ is to adjust the air–fuel ratio to the stoichiometric value to attain the simultaneous conversions of the three main pollutants such as CO, $NO_x$ and hydrocarbons, by providing and absorbing oxygen during fuel-rich and fuel-lean conditions, respectively. In this article, recent advances in the design and development of the sub-catalysts in the autoexhaust catalytic converters are reviewed.

*Keywords:* Cerium oxide; Zirconium oxide; Automotive exhaust catalysts; Oxygen-storage capacity; Catalytic converter

## 1. Background

In recent years, an environmental problem has been highlighted on a world scale. Especially, the effective cleaning of automotive exhaust gas is one of the most important subjects. Since a well-tuned engine still produces many pollutants by the incomplete combustion of the fuel, it has been hoped for a long time that the development of new technologies for controlling the emissions of gaseous pollutants into the atmosphere. Catalytic converters that can reduce the three main pollutants in the automotive exhaust gas such as CO, $NO_x$ and hydrocarbons are referred to as three-way catalysts and they usually consist of precious metals (Pt, Rh, Pd), sub-catalysts ($CeO_2$, $CeO_2$–$ZrO_2$, etc.), andmonolithic ceramic supports (alumina, $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$, etc.) [1].

To establish a high conversion efficiency in the three-way catalyst, the air–fuel ratio (A/F) has to be controlled at the stoichiometric value, about 14.6. The engine A/F is closely monitored by an oxygen sensor device to maintain high conversion efficiency of the pollutants. However, the A/F can widely oscillate around the above optimal value under real car operation and, therefore, the three-way catalysts need sub-catalysts to buffer the oscillation. The most important characteristic of the sub-catalysts is oxygen-storage capacity (OSC). The sub-catalysts in the catalytic converters keep the A/F ratios at their stoichiometric value by providing oxygen to the gas mixture during fuel-rich conditions, and absorbing oxygen in the fuel-lean conditions.

$CeO_2$ has been recognized as a key material of the three-way catalysts since it can release and uptake oxygen owing to the following reversible reaction [2,3].

$$CeO_2 = CeO_{2-x} + (x/2)O_2 \quad (0 \leq x \leq 0.5) \tag{1}$$

In the three-way catalysts, $CeO_2$ works as an oxygen buffer. When the engine is running in the fuel-lean condition, cerium oxide stores oxygen. When the condition changes fuel-rich condition, cerium oxide provides oxygen. The oxidation of $CeO_2$ occurs at room temperature, while the reduction of $CeO_2$ starts at 473 K and is essentially limited to the surface [4]. Therefore, a high surface area is essential for obtaining high OSC. However, pure $CeO_2$ deactivates in its OSC when the exhaust temperatures exceed 1123 K due to sintering of the $CeO_2$ particles and decrease of surface area [5]. As a result, the present converters can attain high conversion only at high temperatures, that is, the present converters cannot eliminate the pollutants at low temperatures when the engine has just started. In accordance with the recent enforce of restrictions, it is essential to develop new sub-catalysts of high activity and high OSC at low temperatures as well as high thermal stability. This is a review of advances in the sub-catalysts in the automotive exhaust cleaning catalysts.

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## 2. Inhibition of sintering at high temperatures

Thermal deactivation of the three-way catalysts is caused by the sintering of fine particles of precious metals and alumina supports as well as $CeO_2$ sintering when the catalysts are subjected at high temperatures for a long time [5]. Sintering of $CeO_2$ facilitates the sintering of the precious metals and the OSC decrease. Therefore, it is very important to stabilize $CeO_2$ when it is used at high temperatures in the driving conditions.

The effect of modification of $CeO_2$ with small amount of other oxides was first reported by Matsumoto and co-workers [6]. They studied the role of the solid solutions of Ce–Zr–O systems as well as Ce–La–O systems as sub catalysts in the three-way catalysts, and found that the addition of La or Zr was very effective to inhibit the sintering of $CeO_2$. Especially, the formation of Ce–Zr mixed oxides is very effective in the inhibition of the sintering.

Recently, a new synthesis of mesoporous high surface area ceria [7–9] and ceria–zirconia [10] has been reported. This method utilizes the reaction of cerium salts under basic conditions with ammonia in the presence of a cationic surfactant. The cationic surfactant acts as a surface area enhancer by incorporation into the hydrous oxide and lowering of the surface tension of water in the pores during drying process. The obtained ceria and ceria–zirconia have enhanced textual and thermal resistance features compared with the conventional samples. Even after calcination at 1173 K, surface areas of $CeO_2$ and $Ce_{0.8}Zr_{0.2}O_2$ are 40 and 56 $m^2/g$, respectively.

## 3. Improvement of oxygen storage capacity

Many studies on $CeO_2$-based materials such as $CeO_2$–$Al_2O_3$ [11], $CeO_2$–$SiO_2$ [12], $CeO_2$–$La_2O_3$ [5,6,11], $CeO_2$–$TbO_x$ [13], and $CeO_2$–$PrO_x$ [14] have been examined to increase the thermal stability and the OSC. Making the solid solution usually promotes the formation of oxygen vacancies and increases the oxygen mobility. The introduction of trivalent ions into the ceria lattice increases the OSC through the creation of oxygen vacancies.

The importance of the application of $CeO_2$–$ZrO_2$ solid solutions to the three-way catalysts was first reported by Ozawa and co-workers [20]. An excellent improvement in the catalytic performance was attained by the increased OSC of $CeO_2$–$ZrO_2$ in $Pt/Al_2O_3$ and practical catalysts. Subsequently, Ranga Rao and co-workers reported that the insertion of $ZrO_2$ into the $CeO_2$ lattice clearly facilitated the reduction process in noble metal-loaded $CeO_2$–$ZrO_2$ [21]. This was attributed to the presence of the supported metal which activated the spilling of hydrogen to the $CeO_2$–$ZrO_2$ support.

The decrease in the reduction temperature is also found in the $CeO_2$-based solid solutions in which $Hf^{4+}$ [13,15] or $Zr^{4+}$ [5,6,16–30] is introduced into $CeO_2$ lattice as a dopant. These were attributed to the high oxygen mobility in the $CeO_2$–$ZrO_2$ or $CeO_2$–$HfO_2$ by the formation of solid solutions. Especially, the introduction of $ZrO_2$ into $CeO_2$ strongly decreases the reduction temperature of ceria through structural modifications of the fluorite type lattice. The substitution of $Ce^{4+}$ (0.97 Å) with $Zr^{4+}$ (0.84 Å) decreases cell volume to lower the activation energy for oxygen ion diffusion. In contrast with pure $CeO_2$, surface area does not influence the reduction behavior of $CeO_2$–$ZrO_2$ solid solutions [22,23]. This indicates that the bulk properties such as phase and structure are more important than the surface.

## 4. Recent advances in $CeO_2$–$ZrO_2$ materials as sub-catalysts in autoexhaust catalytic converters

The introduction of $Zr^{4+}$ into $CeO_2$ lattice also enhances the formation of structural defects. These defects are increased by the mechanical ball-milling and the formed defects seem to be favor of the improvement of the reduction behavior. However, the structural defects created by the milling do not strongly modify the redox behavior of Ce–Zr–O solid solutions [18].

Another interesting feature of $Ce_xZr_{1-x}O_2$ ($x=0.4$–0.6) is the decrease of the reduction temperature after a cycling of high-temperature reduction (1000–1323 K) and subsequent re-oxidation at middle temperatures (700–873 K) [22,23,28–31]. This cycle strongly affects the redox behavior and dramatically increases oxygen storage capacity. The reason for the changes has been explained by slight rearrangement of atoms from their original position, the formation of a cubic κ phase, and the increase in bulk anion mobility into a modified ceria.

The phase characteristics of the $CeO_2$–$ZrO_2$ system are summarized in Table 1 [23]. Below 1273 K, the phase diagram shows a single-phase region of monoclinic structure for the $CeO_2$ molar contents of less than 20%, while for the $CeO_2$ contents higher than 80% a cubic phase was reported [32,33]. In the intermediate region, the true nature of the $CeO_2$–$ZrO_2$ phase diagram is still unidentified due to the presence of many stable and metastable tetragonal phases [32–35]. According to the recent references

Table 1
Classification of the phases in the $CeO_2$–$ZrO_2$ binary system [23]

| Phase | Composition range (% mol Ce) | Tetragnality[a] | Space group |
|---|---|---|---|
| Monoclinic (m) | 0–20 | – | $P2_1/c$ |
| Tetragonal (t) | 20–40 | $>1$ | $P4_2/nmc$ |
| Tetragonal (t′) | 40–65 | $>1$ | $P4_2/nmc$ |
| Tetragonal (t″) | 65–80 | 1 | $P4_2/nmc$ |
| Cubic (c) | 80–100 | 1 | $Fm3m$ |

[a] Defined as axial ratio c/a.

[34,36–39], three different t, t′, and t″ phases can be distinguished on the basis of X-ray diffraction (XRD) and Raman characterization. The t phase is stable and is formed through diffusional phase decomposition. The t′ phase is obtained through a diffusionless transition and it is metastable. The t″ phase is generally referred to as a cubic phase because its XRD pattern is indexed in the cubic *Fm3m* space group.

Pyrochlore $Ce_2Zr_2O_7$ phase is obtained by hydrogen reduction of the t′ phase at high temperatures. In the pyrochlore phase, Ce and Zr ions arrange regularly and this phase was oxidized to metastable κ phase at 700–873 K, maintaining its cation arrangement. The oxygen atoms in the κ phase are relatively unstable compared with those in the tetragonal phase and, therefore, the κ-cubic solid solutions can release oxygen at lower temperatures than t′-tetragonal solid solutions. Recently we prepared $Ce_{0.45}Zr_{0.55}O_2$ solid solutions by means of the thermal decomposition of cerium zirconyl oxalate in an argon flow at 1273 K and subsequent oxidation at 673–873 K in air to obtain the κ phase [40]. Temperature-programmed-reduction (TPR) profile of the obtained $Ce_{0.45}Zr_{0.55}O_2$ is shown in Fig. 1 accompanied by that of the $Ce_{0.45}Zr_{0.55}O_2$ prepared via a redox cycle of hydrogen reduction at 1273 K for 5 h and subsequent air oxidation at 873 K for 2 h. The total amount of released oxygen from the sample prepared from the cerium zirconyl oxalate was 795 $O_2$μmol/(g cat.) which was 1.5 times that of the sample prepared via hydrogen reduction and reoxidation, 545 $O_2$μmol/(g cat.). This is due to the deposition of fine carbon particles produced during the thermal decomposition of the cerium zirconyl oxalate. Since the Gibbs free energy at 1273 K for the reduction of $CeO_2$ is lower than for the reduction by hydrogen [41], the pyrochlore $Ce_2Zr_2O_7$ phase will be produced more effectively by the reduction with carbon particles homogeneously dispersed in an atomic level in the sample than by the hydrogen reduction process. This explanation is also supported by the Raman spectra shown in Fig. 2 which suggests that different structured modifications of the oxygen sublattice may occur between the above two samples.

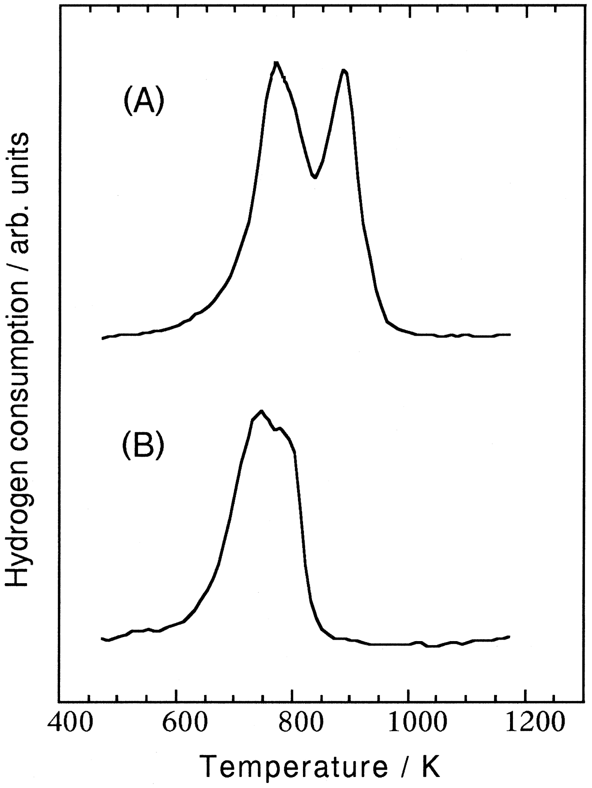

Fig. 1. TPR profiles of the $CeO_2$–$ZrO_2$ powders: (A) TPR profile of the $Ce_{0.45}Zr_{0.55}O_2$ prepared by the thermal decomposition of cerium–zirconyl oxalate in an argon flow at 1273 K and subsequent reoxidation at 673 K. (B) TPR of the $Ce_{0.45}Zr_{0.55}O_2$ prepared by the conventional hydrogen reduction at 1273 K and subsequent reoxidation at 873 K. The TPR measurements were carried out up to 1173 K in a flow of $H_2$ (60 ml/min) using a heating rate of 10 K/min.

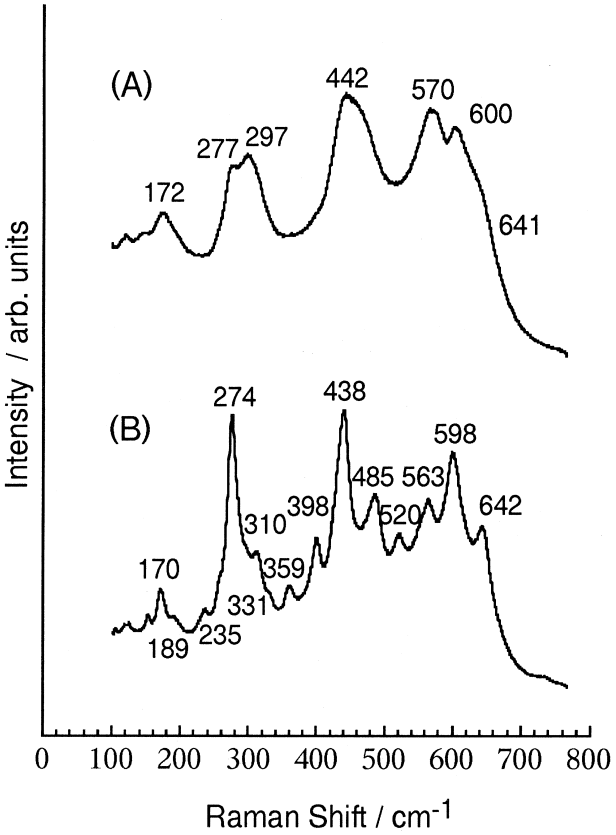

Fig. 2. Raman spectra of the $CeO_2$–$ZrO_2$ powders: (A) $Ce_{0.45}Zr_{0.55}O_2$ prepared from oxalate decomposition in Ar and subsequent reoxidation. (B) $Ce_{0.45}Zr_{0.55}O_2$ prepared by hydrogen reduction and subsequent reoxidation.

## 5. Effect of surface modification — chemical filing

The κ-cubic ceria–zirconia solid solution obtained by the oxidation of the pyrochlore at middle temperatures is a

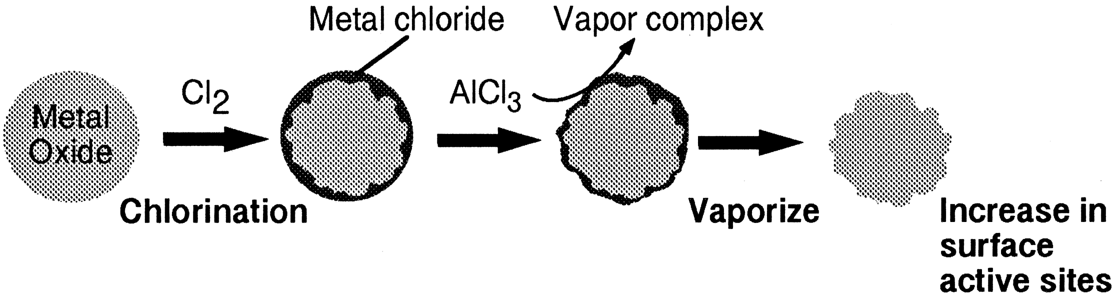

Fig. 3. Illustration of procedures for the filing process based on the chemical vapor transport.

good material. However, it has been reported that the oxygen release temperature became higher after the reoxidation of the cubic ceria–zirconia samples at high temperatures [28–31]. This is due to the phase transformation from kappa or pyrochlore to t*-tetragonal which is more stable than pyrochlore, κ and t′ phases [29,30]. As a result, the oxygen release temperature increases. The increase in oxygen release temperature is a serious problem for the cold-start emission control, since deactivation of the sub-catalysts affects overall catalytic activities. In addition, the close-coupled systems have been developed to solve the cold-start problem. In these systems, the catalytic converters are moved closer to the engine to be warmed up very quickly. But such systems must be designed to with stand extremely high temperatures around 1273 K [42]. Accordingly, ceria-based materials are also required to keep high redox activities after using at high temperatures.

Very recently, a solution to overcome these subjects has been proposed [43]. This concerns surface modification of the pyrochlore samples. It is known that cerium and zirconium chlorides provide vapor phase complexes with aluminum chloride at elevated temperatures [44–46]. The new surface modification technique utilizes the formation of these vapor complexes to remove and modify the top surface of the pyrochlore ceria–zirconia solid solution. This method is called ‘chemical filing’. Application of the above complexes formation was demonstrated for the first time by Adachi and co-workers [47] for the vapor phase extraction and mutual separation of rare earths based on the so-called chemical vapor transport (CVT). Their investigations on the mutual separation and recovery of rare earth from some rare earth containing materials by the CVT process have been reviewed [48].

Fig. 3 shows a schematic representation of the chemical filing process. The first step of the chemical filing process involves the chlorination of the surface of the pyrochlore ceria zirconia sample. The starting ceria–zirconia powders for the chemical filing are prepared by thermal decomposition of cerium zirconyl oxalate in an Ar flow for 5 h. The extent of the chlorination can be controlled by the concentration of the chlorine gas and/or chlorination time, but excess chlorination leads to the decrease of the yield and phase separation. Thecerium and zirconium chlorides partially formed on the surface are eliminated and transported by the formation of gaseous complexes with aluminum chloride and vaporization (2nd step) to form chemically filed oxide powders. The apparatus employed for the chemical filing process is shown in Fig. 4. A ceria–zirconia mixed oxide is placed and partially chlorinated in furnace B. Then, furnace A is heated and aluminum chloride swept off the surface chlorides. As a result, surface modified pyrochlore is obtained. This chemical filing process is carried out at 1273 K to stabilize the surface modification effects at high temperatures.

The chemical filing technique is very effective in modifying the redox property in the low temperature region as shown in Fig. 5 [43]. The TPR profiles of the $Ce_{0.45}Zr_{0.55}O_2$ (trace A) drastically shifted to lower temperatures after the chemical filing (trace B). Moreover, the peak further shifted to lower temperatures after a redox cycle (After the TPR measurement, the $Ce_{0.45}Zr_{0.55}O_2$ was reoxidized in air at 673 K for 5 h and TPR spectrum was measured again.) (trace C). The trace E is the TPR spectrum of the $Ce_{0.45}Zr_{0.55}O_2$ sample prepared by hydrogen reduction at 1273 K and subsequent reoxidation at 873 K denoted the $H_2/O_2$ sample, hereafter). The

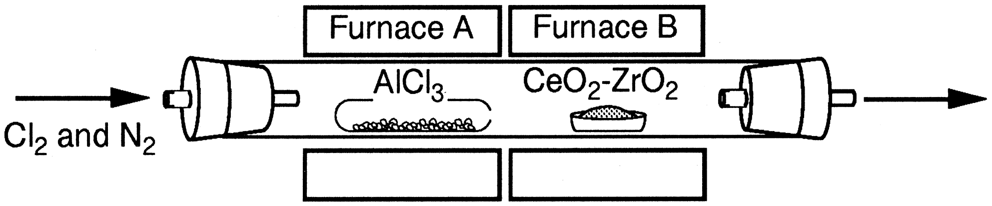

Fig. 4. Assembly of electrical furnaces for the chemical filing process. Furnace A was employed for heating $AlCl_3$, a complex former.

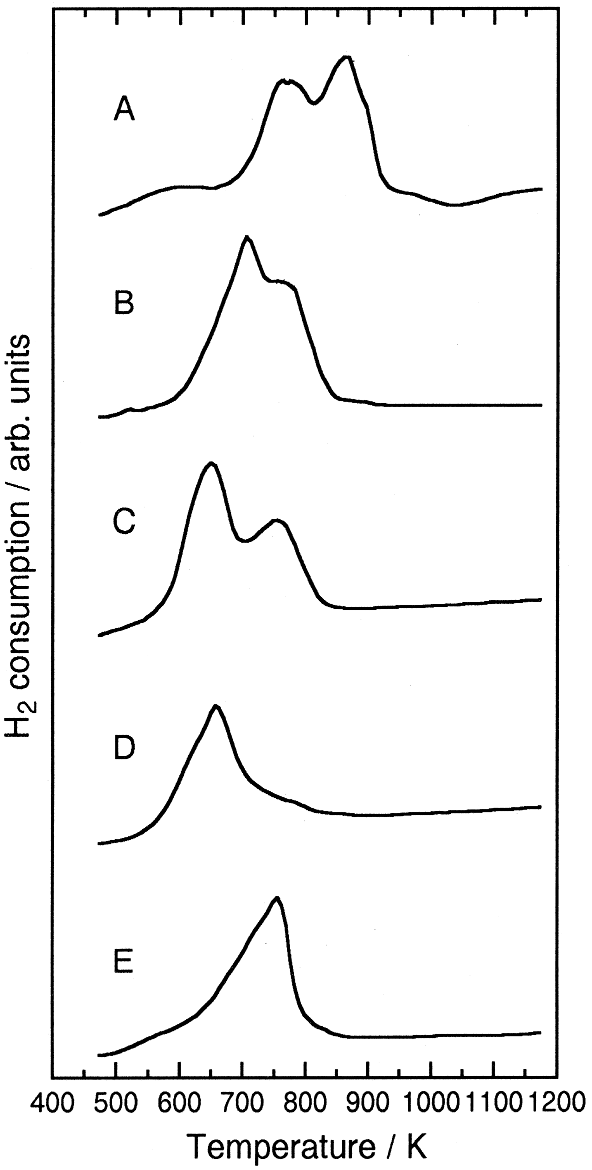

Fig. 5. TPR profiles of $CeO_2$–$ZrO_2$ powders: (A) TPR profile of the $Ce_{0.45}Zr_{0.55}O_2$ prepared from oxalate. (B) TPR of sample A after the chemical filing. (C) TPR of sample after a redox cycle, i.e. an oxidation following the first TPR. (D) TPR of sample after 30 redox cycles, i.e. repetition of the hydrogen reduction and subsequent reoxidation cycle 30 times. (E) TPR of the $Ce_{0.45}Zr_{0.55}O_2$ prepared from hydroxide by hydrogen reduction at 1273 K and subsequent reoxidation at 873 K. The TPR measurements were carried out up to 1273 K in a flow of $H_2$ (80 ml/min) using a heating rate of 5 K/min.

$Ce_{0.45}Zr_{0.55}O_2$ sample obtained by the chemical filing process was reduced at lower temperatures than that given by the conventional $H_2/O_2$ sample.

The peak temperatures and total amount of the oxygen released are summarized in Table 2. Although the amount of oxygen released from the chemically filed sample decreased after 30 hydrogen reduction and subsequent reoxidation cycles at 1273 K (trace D in Fig. 5), the value was still larger than that of the conventional $H_2/O_2$ sample (trace E in Fig. 5). In addition, the oxygen release temperature of the chemically filed sample did not change after the reduction and oxidation cycles at 1273 K, while those of the conventional $H_2/O_2$ samples increased after high temperature oxidation [29–31]. This suggests that the reduction behavior of the chemically filed sample is thermally durable against high temperature redox cycles. The most important request for the $CeO_2$-based materials is oxygen release and uptake behavior at low temperatures when used in automotive exhaust catalysts. The chemically filed $CeO_2$–$ZrO_2$ material prepared in this study showed the reduction behavior at low temperatures and was easily oxidized at 673 K [49].

Table 2
Peak temperatures and $O_2$ release in TPR for $Ce_{0.45}Zr_{0.55}O_2$

| Sample | Peak temperatures (K) | | $O_2$ release ($O_2$ μmol (g cat.)$^{-1}$) |
|---|---|---|---|
| Before chemical filing | 765 | 866 | 795 |
| Chemically filed | 707 | 765 | 772 |
| Chemically filed and 1 redox cycle | 652 | 757 | 728 |
| Chemically filed and 30 redox cycles | 658 | | 567 |
| $H_2/O_2$ sample | 756 | | 545 |

As mentioned above the reason for the high oxygen capacity observed in the $CeO_2$–$ZrO_2$ samples prepared from the cerium zirconyl oxalate has been attributed to both the reduction with carbon uniformly formed in the sample preparation process and the appearance of a cubic phase with an unusual oxygen arrangement by the subsequent oxidation [40]. Since the starting $Ce_{0.45}Zr_{0.55}O_2$ material in the chemical filing process was also prepared from the cerium zirconyl oxalate, it had the cubic phase with the unusual oxygen arrangement. The surface of the $Ce_{0.45}Zr_{0.55}O_2$ sample was chemically filed to a very fine scale using a formation of gaseous complexes and their transportation. Egami and co-workers [50] reported that the presence of nano-size segregated $CeO_2$ phase in contact with $ZrO_2$ or $CeO_2$–$ZrO_2$ enhances the OSC of the ceria–zirconia mixtures. The enhancement of the OSC of the heterogeneous $CeO_2$–$ZrO_2$ was attributed to an unusual nano-scale phase segregation of $CeO_2$ with exposure of high-energy surfaces. In the chemical filing process the specific surface area increased from 3.0 to 5.3 $m^2/g$ after the chemical filing, and excess chemical filing treatment leads to the phase separation into $CeO_2$ and $CeO_2$–$ZrO_2$ [49]. Also, it has been found from Raman spectra measurements that the surface of the chemically filed ceria–zirconia catalyst was covered with a pyrochlore-like compound even after 30 redox cycles at 1273 K [49]. Taking account of these results, it is suggested that the responsibility for the decrease in the reduction temperature by the chemical filing will be due to the formation of active interfacial defects concerning the segregation of a small amount ultrafine $CeO_2$ particles and the stabilization of the pyrochlore phase on the surface during the chemical filing process.

## 6. Summary

In this review, the role of the structural and surface modification for the improvement of OSC which was the most important property as sub-catalysts in the autoexhaust catalytic converters was discussed. The formation of the cubic $CeO_2$–$ZrO_2$ solid solution of κ phase based on the pyrochlore structure is very effective to the enhancement of the OSC and to decrease the reduction temperature. However, the reduction temperature of the κ phase prepared by the conventional process increases after oxidation at high temperatures. Surface modification of the κ phase by the chemical filing process using the formation of vapor complexes is one of the solutions to this problem. This process named 'chemical filing' is effective to maintain the low temperature reduction behavior of the κ phase even after oxidation and reduction cycles at high temperatures. The characteristic is the requirement for the next generation of automotive exhaust catalysts.

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