Redox Behavior of Ceria−Zirconia Solid Solutions Modified by the Chemical Filing Process

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In the ceria−zirconia system, two kinds of preparation methods using oxalic acid or hydrazine monohydrate have been investigated to improve oxygen release and storage properties at low temperatures. These processes consist of a reduction process and surface modification. The redcutants were carbon particles produced by thermal decomposition of oxalate or a mixture of hydrazine and hydrogen produced by decomposition of hydrazine monohydrate, and the surface modification was carried out by the calcination of the obtained powders with ammonium chloride in air at 1273 K for 1 h. Cerium and zirconium chlorides produced on the surface of the solid solutions vaporized to form a chemically filed surface. As a result of the treatment, the ceria−zirconia solid solutions released a larger amount of oxygen at lower temperatures. The oxygen storage capacity of the samples measured by a pulse technique also increased after the treatment. The redox properties of the chemically filed samples have been maintained even after reduction and reoxidation aging at 1273 K for many times, indicating thermal durability of the redox activity of the catalysts.

Introduction

Ceria-based materials, especially ceria−zirconia mixed oxides, are very important components of promoters for automotive three-way catalysts (TWCs) because of their oxygen storage capacity (OSC) based on the redox behavior between Ce^{3+} and Ce^{4+}.[1−7] They play a role in widening the apparent air/fuel ratio where the TWCs act effectively in the converters. Generally, higher conversion efficiencies are observed with higher OSCs of the promoter.[8] As restrictions for automotive exhaust gas become stricter, the need to remove the pollutants, especially at low temperatures, increase year by year. A major problem of the catalytic converters is that a catalyst needs to reach about 600 K to attain significant conversions of the pollutants, particularly for the hydrocarbons.[2] One solution is to move converters closer to the engine to be warmed very quickly because of their close proximity to the engine. This system is called a close-coupled catalyst. In such systems, however, the catalysts must be designed to withstand extremely high temperatures because the converters experience up to 1273−1373 K.

As a work on this line, many attempts have been made to enhance redox property of ceria−zirconia solid solutions, and it is well-known that the redox behavior is highly sensitive to the kind of preparation and pretreatment processes.[9−22] Among these studies, it has

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been accepted that the ceria−zirconia mixed oxides prepared via severe reducing conditions (1223−1373 K) followed by oxidation at mild temperatures (623−873 K) have good oxygen release and storage capacity at low temperatures.

In this study, we have employed two kinds of reductants such as carbon, which is produced by thermal decomposition of cerium−zirconium mixed oxalate, and a mixture of hydrazine and hydrogen produced by decomposition of hydrazine monohydrate[23,24] to attain severe reducing conditions. In addition, we have reported in the previous studies that a surface treatment, which consists of surface chlorination using chlorine gas and elimination of the formed metal chlorides by chemical vapor transport, lowered the oxygen release temperature of the CeO_2-ZrO_2 mixed oxides prepared by the thermal decomposition of cerium zirconyl oxalate.[25−27] Thermostability of the redox activity at low temperatures was improved by the surface treatment. We named this process “chemical filing”.

However, it is more convenient for modification of the catalysts to utilize solid-state reaction than gas−solid reaction. Ammonium chloride (NH_4Cl) has been used for synthesis of rare earth chlorides from the corresponding oxides[28] and have the advantage over the other solid chlorinating agents in that no metal component remains after the chlorination reaction. In this paper, we report on the effect of the surface treatment, which consists of surface chlorination using ammonium chloride and elimination of the formed metal chlorides by vaporization, on the reduction behavior of $Ce_{0.5}Zr_{0.5}O_2$ solid solutions.

Experimental Section

Aqueous solutions of cerium nitrate and zirconyl nitrate (>99.9% in purity) were supplied by the Shin-Nippon Kinzoku Kagaku Co., Ltd. Oxalic acid and hydrazine monohydrate were purchased from Wako Pure Chemical and used as received. Two methods were used to synthesize the starting $Ce_{0.5}Zr_{0.5}O_2$ powders. The first method was thermal decomposition of a cerium zirconyl mixed oxalate, $Ce_2(ZrO)_2(C_2O_4)_5 \cdot nH_2O$, which was precipitated by adding a mixture of 1.0 M aqueous solutions of cerium nitrate and zirconyl nitrate with a Ce/Zr ratio of 1/1 to 0.5 M oxalic acid solution, adjusting the pH value of the solution to 2 with ammonium hydroxide. The precipitate was washed with deionized water several times, dried at 353 K overnight, and heated in an argon flow (30 mL min^{-1}) at 1273 K for 5 h. During the heating fine carbon particles were produced and worked as a reductant.

The second method of the preparation was coprecipitation by hydrazine monohydrate. The reason for using hydrazine monohydrate as a precipitant is that hydrazine is a base and a powerful reducing agent to prevent oxidation of Ce^{3+} to Ce^{4+} during the preparation process.[23] Hydrazine is stable at room temperature but at elevated temperature it decomposes into nitrogen and hydrogen on metal oxide.[24]

The equimolar mixture of aqueous solutions of cerium and zirconyl nitrates was added dropwise to an excess amount of hydrazine monohydrate at room temperature with stirring. The suspension was aged for 4 days at the same temperature. After the mixture was centrifuged at 3000 rpm, the wet precipitate was dried at 353 K in an argon flow for 3 h and subsequently heated at 1273 K in the same conditions for 5 h.

The chemical filing treatment using NH_4Cl was carried out as follows. The ceria−zirconia powders synthesized from those above processes were mixed with NH_4Cl in an alumina mortar for 15 min, respectively. The mass ratio of the ceria−zirconia powder to NH_4Cl was adjusted to 2 to 1. The mixtures were heated at a heating rate of 200 K h^{-1} to 1273 K in air and held at this temperature for 1 h. The chlorination occurred at the surface of the starting material in contact with NH_4Cl and the produced metal chlorides vaporized with excess ammonium chloride. Hereafter, the samples prepared from oxalic acid and hydrazine monohydrate are denoted "oxa-CeO_2-ZrO_2“ and ”hyd-CeO_2-ZrO_2," respectively.

X-ray powder diffraction patterns were measured using a MAC Science M18XHF-SHA diffractometer using Cu Kα radiation. FT-Raman spectra were obtained on the Ultimate Raman System (Kaiser Optical Systems, HoloProbe). The spectra were excited with an Ar ion laser operating at 633-nm wavelength, and the laser power was 5 mW. The BET surface area of the samples was measured with a Mircometrics FlowSorb II 2300 instrument. Bulk and surface compositions of the samples were determined by an X-ray fluorescent spectrometer (Rigaku System 3270A) and an X-ray photoelectron spectroscopy apparatus (Physical Electronics, model-5500MT), respectively. High-resolution electron microscopic (HREM) images were recorded using a JEOL4000-EX microscope operating at 400 kV. Samples were prepared by dipping a 3-mm holey carbon copper grid into an ultrasonic dispersion of the oxide powder in ethanol.

Reduction behavior was examined by temperature-programmed reduction (TPR) experiments using a thermal conductivity detector of a gas chromatograph (Shimadzu, GC-8A). To minimize the effects of adsorbed species on TPR, all the samples were pretreated in He (80 mL min^{-1}) at 873 K for 2 h before the initial TPR experiment. The TPR characterization was performed on 0.03 g of catalyst under a H_2 flow with a flow rate of 80 mL min^{-1} from room temperature to 1273 K (heating rate 10 K min^{-1}). After the TPR measurement, the sample was outgassed under a He flow at 1273 K for 30 min and cooled to 700 K, where oxygen uptake was measured by a pulse technique. Pulses of O_2 (0.2 mL) were injected into the flow of He passing through the sample until the breakthrough point was attained. Low-temperature OSC values of the fresh and chemically filed samples were measured by the same pulse technique. Before the O_2 injection, the sample was reduced under a H_2 flow at 700 K for 30 min and then the sample was outgassed under a He flow at the same temperature.

Catalytic measurements of the CeO_2-ZrO_2 mixed oxides for methane combustion were carried out on a 500-mg sample in a quartz microreactor (8-mm i.d.). The samples were calcined under flowing helium at 573 K for 3 h prior to the catalytic activity measurement. The inlet gas composition was CH_4 (1 vol %) and O_2 (4 vol %) with He as balance. The flow rate was adjusted to have a space velocity of 20 000 h^{-1}. The inlet and outlet gas composition was measured with a gas chromatograph (Shimadzu GC-8A).

Results and Discussion

Characterization of the Chemically Filed Ceria−Zirconia Solid Solutions. Table 1 summarizes the surface and bulk composition of the ceria−zirconia powders after the chemical filing treatment, which were determined by X-ray photoelectron spectroscopy (XPS) and X-ray fluorometry, respectively. X-ray fluorescence analysis showed that all the CeO_2-ZrO_2 solid solutions contained only cerium and zirconium. For all samples,

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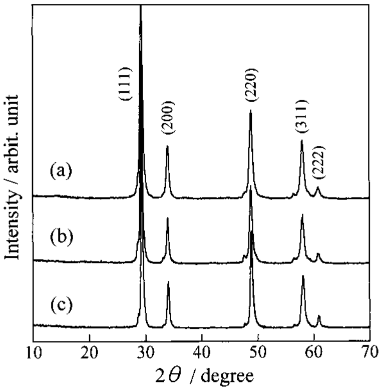

Figure 1. X-ray diffraction patterns of oxa-CeO_2-ZrO_2 solid solutions, which are fresh (a), chemically filed (b), and redox-aged (c).

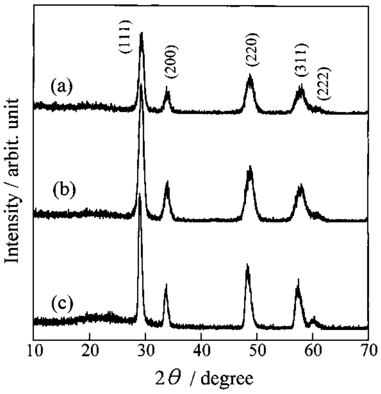

Figure 2. X-ray diffraction patterns of hyd-CeO_2-ZrO_2 solid solutions, which are fresh (a), chemically filed (b), and redox-aged (c).

Table 1. Bulk and Surface Compositions of Oxa- and Hyd-CeO_2-ZrO_2 Powders before and after the Surface Treatment

sample	bulk comp	surface comp
fresh oxa-CeO_2-ZrO_2	$Ce_{0.47}Zr_{0.53}O_2$	$Ce_{0.55}Zr_{0.45}O_2$
chemically filed oxa-CeO_2-ZrO_2	$Ce_{0.47}Zr_{0.53}O_2$	$Ce_{0.57}Zr_{0.43}O_2$
fresh hyd-CeO_2-ZrO_2	$Ce_{0.49}Zr_{0.51}O_2$	$Ce_{0.55}Zr_{0.45}O_2$
chemically filed hyd-CeO_2-ZrO_2	$Ce_{0.49}Zr_{0.51}O_2$	$Ce_{0.59}Zr_{0.41}O_2$

surface enrichment of cerium was observed and it proceeded by the chemical filing process. Because no peaks related to chlorine and nitrogen were observed in the X-ray fluorescent and the XPS spectra, no ammonium salts, chlorides, and oxychlorides remained in the samples after the treatment.

Figure 1 compares X-ray diffraction (XRD) patterns of the oxa-CeO_2-ZrO_2 powders with and without the chemical filing treatment with ammonium chloride at 1273 K, respectively. The diffraction pattern of the chemically filed samples showed no peaks assigned to NH_4Cl. Both samples had the cubic fluorite structure, and no apparent changes of intensities and positions of the peaks were observed by the surface treatment. Figure 2 shows the XRD results of the hyd-CeO_2-ZrO_2. This sample also showed a similar tendency; however, the crystallinity of these samples was less than that of the CeO_2-ZrO_2 samples. The surface area of these samples is also summarized in Table 2. The surface area of the hyd-CeO_2-ZrO_2 was larger than that of the oxa-CeO_2-ZrO_2, and these increased after the chlorination.

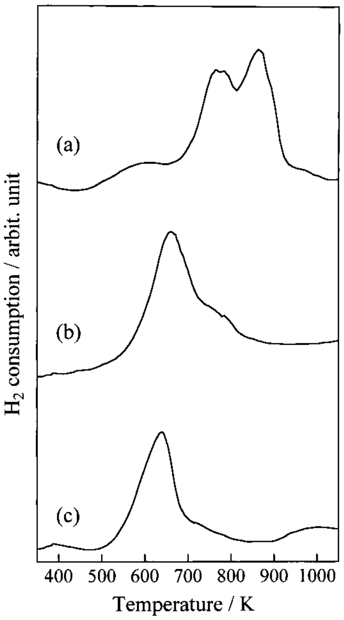

Figure 3. TPR profile of oxa-CeO_2-ZrO_2 solid solutions, which are fresh (a), chemically filed (b), and redox-aged (c).

The starting CeO_2-ZrO_2 powders prepared in an argon flow have a pyrochlore-related cubic phase.[18,27] From analogy with that of binary rare earth oxides, the following equation is assumed for the chlorination of pyrochlore-type $Ce_2Zr_2O_7$ with NH_4Cl:

$$Ce_2Zr_2O_7 + 14NH_4Cl \rightarrow 2CeCl_3 + 2ZrCl_4 + 14NH_3 + 7H_2O$$

The chlorination proceeds in the temperature range from 500 to 700 K as in the case of binary rare earth oxides.[28] Ammonium chloride decomposes into NH_3 and HCl and vaporizes at higher temperatures. While $ZrCl_4$ formed by the chlorination has extremely high vapor pressure at about 600 K and is removed from the reaction zone by immediate volatilization, $CeCl_3$ has very low vapor pressure at the same temperature and is oxidized in air to form CeO_2. This difference of vapor pressure induces the enhancement of the cerium enrichment by the chemical filing process.

Temperature-Programmed Reduction and OSC Measurements. TPR profiles of fresh and chemically filed oxa- and hyd-CeO_2-ZrO_2 mixed oxides are reported in Figures 3 and 4, respectively. The fresh oxa-sample shows three peaks, whereas the others show essentially one or two peaks. The temperatures of the peak maximum and shoulders are reported in Table 2 with the overall oxygen uptakes (total OSC) measured after TPR experiments.

A fresh oxa-CeO_2-ZrO_2 sample features two major peaks around 770 and 870 K and a minor one around 600 K. The lowest minor peak corresponds to the reduction of the surface and bulk, and the remaining two peaks have been attributed to the reduction process of the bulk.[27] The chemical filing treatment leading to this sample depresses the reduction at lower temperatures and the main reduction peak becomes a sing one. The main reduction temperature was 658 K with a shoulder peak around 750 K. This chemical filing treatment increased the surface area from 3.0 to 6.8 m^2 g^{-1}.

Table 2. Peak Temperature, Oxygen Storage Capacity, and Specific Surface Area of Oxa- and Hyd-CeO_2-ZrO_2 Powders before and after the Chemical Filing

sample	peak temp/K	total OSC/μmol g^{-1}	surface area/m^2 g^{-1}
fresh oxa-CeO_2-ZrO_2	768, 865	741	3.0
chemically filed oxa-CeO_2-ZrO_2	658	737	6.8
chemically filed and redox-aged oxa-CeO_2-ZrO_2	638	701	3.0
fresh hyd-CeO_2-ZrO_2	755	621	15.3
chemically filed hyd-CeO_2-ZrO_2	670	638	15.2
chemically filed and redox-aged hyd-CeO_2-ZrO_2	666	549	7.4

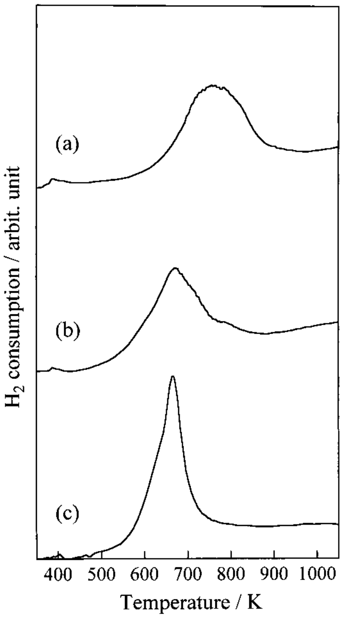

Figure 4. TPR profile of hyd-CeO_2-ZrO_2 solid solutions, which are fresh (a), chemically filed (b), and redox-aged (c).

Similar behavior was also observed in the case of the hyd-CeO_2-ZrO_2 sample. However, total OSC values of them are relatively lower than those given by the oxa-CeO_2-ZrO_2 samples. It is reasonable to think that this is due to the difference in crystallinity of these two samples because it is obvious from the results of XRD and specific surface area that crystallinity of the oxa-sample is higher than that of the hyd-sample. However, the difference in preparation process cannot be excluded as the origin of these results. The hyd-CeO_2-ZrO_2 sample was prepared from cerium−zirconium mixed hydroxide partially containing a $Ce-NH_2NH_2-Zr$ bond by hydrazine monohydrate.[29−31] On the other hand, the oxa-CeO_2-ZrO_2 solid solution was prepared by the decomposition of cerium−zirconyl mixed oxalate in an inert gas flow producing fine carbon particles. The reducing agents were a mixture of hydrazine and hydrogen in the former processes and carbon particles in the latter.

As mentioned in the Introduction, it is widely accepted that the redox aging that consists of reduction at high temperatures (1273−1323 K) and reoxidation at mild temperatures reduces the oxygen release temperature.[10−22] In this activation process, the total OSC of the sample is in proportion to the reduction temperature.[14,15] Accordingly, it is considered that the oxide sample prepared from oxalate was more activated by the carbon particles than the sample prepared via reduction by a mixture of hydrazine and hydrogen. Since the Gibbs free energy at 1273 K for the reduction of CeO_2 to Ce_2O_3 by carbon was lower than that for the reduction by hydrogen,[32] which is produced by the decomposition of hydrazine, thermal decomposition of the oxalate in an argon atmosphere would more effectively produce the severe reducing conditions than the other reduction process.

Table 3. Oxygen Storage Capacity of CeO_2-ZrO_2 Solid Solutions after Reduction at 700 K As Measured from O_2 Pulses at 700 K

sample	OSC after reduc. at 700 K/μmol g^{-1}
fresh oxa-CeO_2-ZrO_2	129
chemically filed oxa-CeO_2-ZrO_2	558
chemically filed and redox-aged oxa-CeO_2-ZrO_2	540
fresh hyd-CeO_2-ZrO_2	142
chemically filed hyd-CeO_2-ZrO_2	400
chemically filed and redox-aged hyd-CeO_2-ZrO_2	446

Low-temperature OSC values of the fresh and chemically filed samples after reduction at 700 K were also measured by the O_2 pulse technique (Table 3). Except for the fresh sample, the low-temperature OSC values of the oxa-CeO_2-ZrO_2 samples were higher than those of the “hyd” solid solution after reduction at low temperatures since reduction of the chemically filed oxa-sample was easier than that of the chemically filed hyd-sample.

As mentioned in the previous section, the chemical filing process stimulates vaporization of zirconium on the surface of the solid solution. The surface defects produced by the evaporation of zirconium are expected to play an important role in the enhancement of the oxygen release and storage property. To identify this consideration, we observed the surface of the chemically filed and unfilled samples using HREM. As shown in Figure 5, it became clear that the chemical filing process produced cerium oxide ultrafine particles on the nanometer scale on a part of the CeO_2-ZrO_2 surface. It has been recognized that the presence of a nanoscale segregated CeO_2 phase in close contact with CeO_2-ZrO_2 enhances the oxygen release and storage performance of ceria−zirconia mixtures.[33] Therefore, it is concluded that the formation of trace amounts of CeO_2 ultrafine particles with the evolution of surface defects was the reason for the improvement of the oxygen release and storage properties by use of the chemical filing method.

Catalytic Activities. The catalytic activities of the CeO_2-ZrO_2 mixed oxides have been carried out to study

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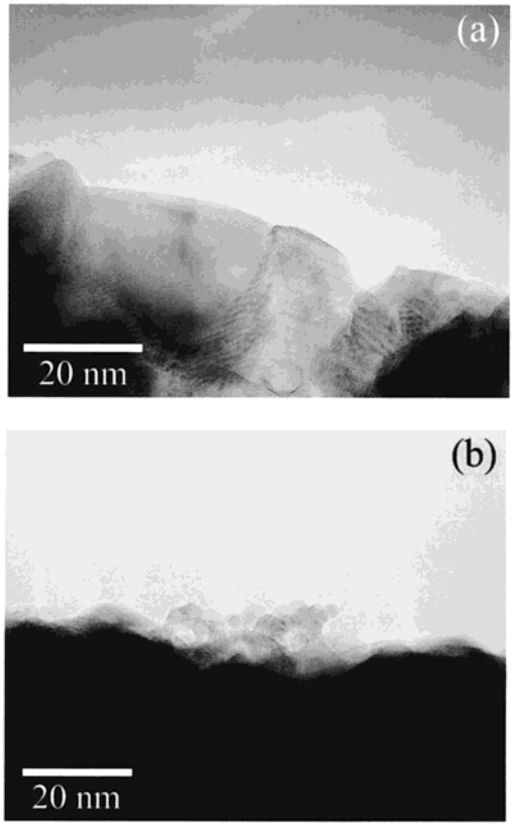

Figure 5. HREM images of oxa-CeO_2−ZrO_2 solid solutions, which are fresh (a) and chemically filed (b).

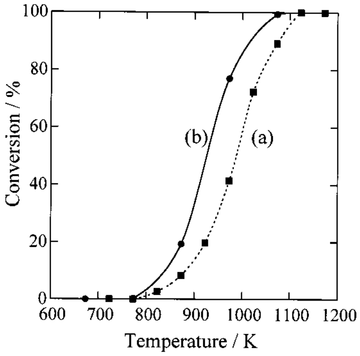

Figure 6. Catalytic activity in the oxidation of methane over oxa-CeO_2−ZrO_2 solid solutions, which are fresh (a) and chemically filed (b).

the effect of chemical filing on the combustion of methane. The results at different temperatures are reported in Figure 6. It is shown that the activity is enhanced by the surface modification. The light-off temperature of half conversion (T_{50}) varied from 987 to 925 K by the chemical filing process.

Catalytic activities of CeO_2-based solid solutions for methane combustion have been investigated.[34] The activities of CeO_2−ZrO_2 solid solutions that showed reduction at low temperatures were greatly larger than those of the others. It is suggested that the increase in the oxidation activity is related to the higher oxygen mobility at low temperature and the lower reduction temperature of the CeO_2-based materials.

In addition, the correlation between low-temperature reduction peaks in the TPR profiles and three-way activity has been established for the CeO_2-based catalysts.[35−37] The disappearance of low-temperature peaks in TPR spectra causes a significant deactivation of the catalysis for the conversion of methane,[37] carbon monoxide, and nitrogen monoxide.[35,36] Taking into account these results, it is reasonable to consider that the oxygen release property in low temperatures plays an important role in the oxidation of hydrocarbon at lower temperatures.

Effect of Redox Aging on the Oxygen Release and Storage Properties. The effect of continuous reduction and reoxidation cycles on the structure and reduction behavior was investigated for oxa- and hyd-CeO_2−ZrO_2 powders. The reduction was carried out in a flow of hydrogen at a heating rate of 10 K min^{-1} up to 1273 K, and then the sample was held at this temperature for 10 min. After the atmosphere was replaced with helium for 15 min, the sample was reoxidized in a flow of air for 10 min at 1273 K. The TPR profiles of the chemically filed samples after the reduction and reoxidation aging took place 10 times are also compared in Figures 3 and 4. The peak temperature in the TPR and the overall oxygen storage capacity of the recycled samples are summarized in Table 2. After the redox aging, the peak temperature remains unchanged, although the OSC slightly decreased. This result suggests that the redox property of the chemically filed sample is relatively stable since it has been reported that the conventionally aged sample featured the shift of the reduction peak to higher temperatures after oxidation at high temperatures.[13]

The oxygen release peak temperature of the chemically filed oxa-CeO_2−ZrO_2 sample with NH_4Cl was about 50 K lower than that of the chemically filed sample with chlorine gas.[27] This is due to the difference of the two kinds of the chemical filing treatment in the mechanism. In the chemical filing treatment with chlorine gas, chlorination proceeds not only in the surface but also in the inner part of the sample by diffusion of Cl_2. In solid-state chemical filing, on the other hand, the sample is surrounded by NH_4Cl, and the surface chlorination proceeds more homogeneously. The surface area of the chemically filed CeO_2−ZrO_2 mixed oxides with NH_4Cl (6.8 m^2 g^{-1}) was larger than that of the chemically filed sample with chlorine gas (5.3 m^2 g^{-1}), despite the heating of the former sample in more severe conditions than those of the latter sample.

Raman Spectroscopy of the Surfaces. To have some insight into the origin of the above results, modifications of the oxygen sublattice were investigated by Raman spectroscopy. Figures 7 and 8 show Raman spectra of fresh, chemically filed, and redox-aged oxa- and hyd-CeO_2−ZrO_2 samples, respectively. The Raman spectrum of the fresh oxa-sample features six strong bands centered at 272, 304, 446, 470, 578, and 611 cm^{-1} and a shoulder one at about 640 cm^{-1}. This spectrum

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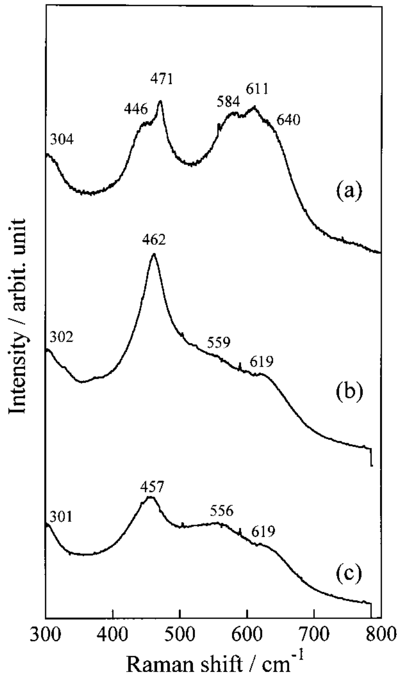

Figure 7. Raman spectra of oxa-CeO_2−ZrO_2 solid solutions, which are fresh (a), chemically filed (b), and redox-aged (c).

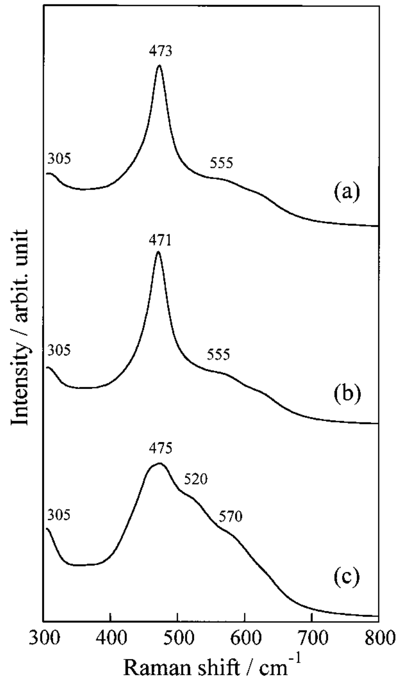

Figure 8. Raman spectra of hyd-CeO_2−ZrO_2 solid solutions, which are fresh (a), chemically filed (b), and redox-aged (c).

is similar to that of the K-phase, which is prepared by reduction at high temperatures and subsequent reoxidation at mild temperatures of a solid-state synthesized CeO_2−ZrO_2 (Ce/Zr = 1/1) solid solution.[20−22] The fresh hyd-CeO_2−ZrO_2 sample showed a strong band at 473 cm^{-1}, which is attributed to the single Raman active mode of F_{2g} symmetry allowed for the fluorite structure.[38] The presence of weak bands at 305 cm^{-1} has been attributed to a partial breaking of $Fm3m$ symmetry due to a tetragonal displacement of the oxygen atoms from the ideal tetrahedral sites.[39] Such a spectral feature is attributed to the presence of a t'' phase, which is a tetragonal phase with the axial ratio a/c equal to 1.

The striking effects of the chemical filing treatment are observed on the Raman spectra of the oxa-CeO_2−ZrO_2 (Figure 5, trace b) sample. The bands at 584 and 611 cm^{-1} extremely decreased their intensity and those at 446 and 471 cm^{-1} combined to a single one at 462 cm^{-1}, and the overall spectrum corresponded to the t'' phase. On the other hand, the Raman spectra of the hyd-CeO_2−ZrO_2 (Figure 5, trace b) solid solution almost was unchanged. Although the same phase was formed in the oxa- and hyd-samples, the OSC of the former was larger than that of the latter. This is attributed to the difference in preparation method and crystallinity of these two samples, as discussed above.

Redox aging at high temperatures after the chemical filing treatment induces noticeable modifications both of the Raman spectra. The decrease in intensity of the F_{2g} mode around 470 cm^{-1} after the redox aging is consistent with the breaking of the local symmetry around the cations, suggesting a high structural disorder in the cubic oxygen sublattice.[40,41] There are few dissimilarities in XRD patterns previously shown in Figure 1, but there is a clear difference in the spectra between the redox-aged oxa- and hyd-samples. Typically, the F_{2g} mode of oxa-CeO_2−ZrO_2 shifts to somewhat lower frequencies compared to that of hyd-CeO_2−ZrO_2 (475 cm^{-1}). The same tendency was observed in the frequencies of the shoulder peaks. These indicate that the two different phases with different symmetries are formed upon redox aging, and these are attributed to t'_{meta} and t' phases for the oxa- and hyd-samples, respectively.[22] The t'_{meta} is a metastable tetragonal phase and has a large oxygen storage capacity, but usually it transformed into a more stable t' phase by heating above 1173 K under an O_2 atmosphere.[22] In our case, however, this t'_{meta} phase was stabilized and did not change into the t' phase even after oxidation at 1273 K. Accordingly, we suggest that such a phenomenon, which generates and stabilizes the t'_{meta} phase, could be responsible for the improved redox properties (low reduction temperature and high oxygen capacity) of the chemically filed oxa-CeO_2−ZrO_2 sample. The reason for the stabilization of the t'_{meta} phase was unclear, but work is in progress to elucidate this point.

Conclusions

The chemical filing process is a promising method for preparation of CeO_2−ZrO_2 mixed oxide catalysts with improved oxygen release properties and durability. This filing proceeded by chlorination with ammonium chloride followed by the dominant vaporization of formed zirconium chlorides. The vaporization produced ultrafine ceria particles on the surface of the CeO_2−ZrO_2 mixed oxide. As a result, the reduction temperatures of the chemically filed samples became lower than those of the nonfiled ones without decreasing in the amount

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of the released oxygen. The results of Raman spectra showed that the repetitive reduction/reoxidation aging at 1273 K affected the reduction temperature of the chemically filed samples. After the aging, the redox property of the sample prepared from oxalate was superior to that prepared using hydrazine monohydrate. The reason for the better redox activity was attributed to the difference in reduction agent and crystallinity of these two samples and the stabilization of the t'_{meta} phase.

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