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Redox Behavior of Surface-Modified CeO_2-ZrO_2 Catalysts by Chemical Filing Process

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Surface modification of CeO_2-ZrO_2 solid solutions took place using formation and transport of volatile vapor complexes such as $AlCl_3-CeCl_3$ and $AlCl_3-ZrCl_4$, which was denoted as "chemical filing." XPS analysis showed surface Ce enrichment, and transmission electron microscopy and Raman spectra revealed that a defective phase was formed on the surface of the samples by the chemical filing. The reduction temperature of the samples after the chemical filing was about 50 K lower than that of the fresh sample and further decreased by a reduction/reoxidation cycle. The redox property of the chemically filed sample was maintained even after the redox cycles at high temperatures, indicating its excellent durability compared to the solid solution prepared by a conventional procedure.

Introduction

Automotive three-way catalysts (TWCs) convert three main pollutants, CO, hydrocarbon (HC), and NO_x, to CO_2, H_2O, and N_2, simultaneously.[1] However, the air-to-fuel ratio in the catalytic converters needs to be kept near the stoichiometric value (about 14.6) to attain the simultaneous conversion. Cerium oxide (ceria) is an important component of promoters for TWCs[2,3] because of its oxygen storage capacity (OSC), based on the redox behavior between Ce^{3+} and Ce^{4+}: ceria plays a role in widening the apparent air/fuel ratio where the catalysts act effectively, by releasing oxygen in "reducing conditions" and storing oxygen in "oxidizing conditions". In recent years, the incorporation of Zr into CeO_2 lattices has been reported to improve thermal stability as well as oxygen storage capacity.[4,5] The subject in the promoters of the TWCs is improvement in the oxygen release property at lower temperatures. Whereas oxidation of the present promotor readily proceeds even at room temperature, its reduction requires relatively higher temperatures above 600 K. As restrictions for automotive exhaust gas become stricter, the need to remove these exhaust gas, especially in low temperatures, increase year by year. Many attempts have been made for lowering the oxygen release temperature of CeO_2-ZrO_2 solid solutions.[6−18] One of the important factors, which has an effect on the oxygen release property, is the textural property of the solid solution. It was shown that $Ce_{0.5}Zr_{0.5}O_2$ solid solution with high surface area, which was derived by sol−gel route, released oxygen at much lower temperature than that with low surface area prepared by the solid-state reaction.[9,10] Doping of trivalent ions such as Y, La, and Ga into CeO_2-ZrO_2 solid solutions facilitates the diffusion of oxygen in the lattice by formation of anion defects and decreases the reduction temperature of the solid solutions.[11,12] Loading of noble metals on the solid solutions also improves the oxygen release property by a synergetic effect between the noble metals and the supports.[13] In addition to these modification, it is widely accepted that the redox cycles

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of reduction at high temperatures (1273−1323 K) and reoxidation at mild temperatures (700−873 K) reduce the oxygen release temperature[10,14−18] even for CeO_2−ZrO_2 solid solutions synthesized by conventional methods such as coprecipitation and solid-state reaction. Although the oxygen release property depends on both the properties of bulk and surface, there have been few studies on the surface modification of CeO_2−ZrO_2 solid solutions.

Metal oxides are converted into the corresponding chlorides by chlorine gas in the presence of carbon as a reducing agent.[19] Although vaporization of less volatile metal chlorides, such as rare-earth chlorides, requires considerably higher temperatures, their volatility are largely enhanced by the reversible reaction with aluminum chloride to form halogen-bridged vapor complexes,[20−22]

$$RCl_3\ (s,\ l) + {}^{n}/_{2}Al_2Cl_6\ (g) = RAl_nCl_{3+3n}\ (g) \qquad (n = 1-4) \quad (1)$$

where R denotes rare earth elements. Therefore, metal components in the oxides are volatilized through the chlorination and the subsequent formation of the vapor complexes. It seems that chlorination of mixed oxides heterogeneously occurs because of the difference of each component in reactivity with chlorine. If the condition of chlorination could be controlled so that only the surface of samples is chlorinated, this heterogeneity in chlorination induces formation of a rough and defective surface phase with a composition and structure different from those of bulk. This surface treatment process, which we named "chemical filing", is promising for the surface modification of catalytic materials. In addition to the reduction behavior at low temperatures, improvement in thermostability is also expected for long-term, high-temperature chemical filing treatment.

It was shown that a CeO_2−ZrO_2 solid solution prepared by thermal decomposition of an oxalate precursor had an excellent oxygen storage capacity.[23] However, its oxygen release temperature was relatively high. We previously observed that the chemical filing process greatly decreased the oxygen release temperature of the oxalate-derived CeO_2−ZrO_2 solid solution.[24] The aims of this work are to investigate the effects of the chemical filing treatment on surface and bulk structures of CeO_2−ZrO_2 solid solutions and to elucidate the mechanism of the modification on oxygen release ability.

Experimental Section

Aqueous solutions of cerium nitrate $Ce(NO_3)_3$ and zirconyl nitrate $ZrO(NO_3)_2$ (>99.9% in purity) were obtained from Shin-Nippon Kinzoku Kagaku Co., Ltd. Aluminum chloride (99.99%) and active carbon were purchased from Aldrich and Nacalai Tesque, Inc., respectively, and used as received.

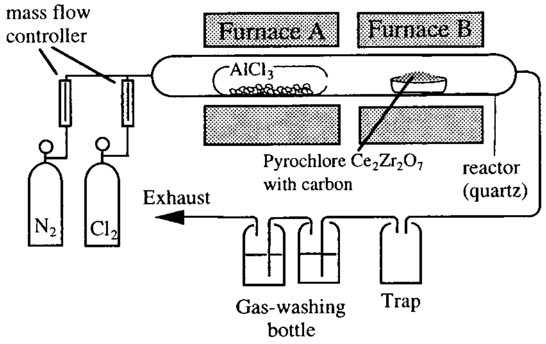

Figure 1. Schematic diagram of the apparatus for the chemical filing process.

Three methods were used to prepare the starting CeO_2−ZrO_2 powders. The first method was thermal decomposition of a Ce−Zr mixed oxalate according to a procedure published previously.[23] Briefly, the precipitate of cerium zirconyl oxalate $Ce_2(ZrO)_2(C_2O_4)_5{\cdot}nH_2O$ was formed 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 and subsequently 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 Ar flow at 1273 K for 5 h to be converted into black powder. The sample obtained by this method is denoted "oxa-CeO_2−ZrO_2." The second method of the preparation was coprecipitation of Ce and Zr hydroxides. First, the equimolar mixture of aqueous solutions of cerium and zirconyl nitrates was added to excess ammonium hydroxide. After being washed and dried in a manner similar to the first method, the precipitate was heated in air at 1173 K for 5 h. This sample is denoted "cp-CeO_2−ZrO_2." The third method is reduction of the cp-CeO_2−ZrO_2 in an H_2 flow at 1323 K for 5 h, with subsequent reoxidation in air at 873 K for 5 h. The obtained sample is denoted as "reduced/reoxidized CeO_2−ZrO_2."

These starting CeO_2−ZrO_2 powders were subjected to the chemical filing processes. The chemical filing process consists of two steps: chlorination and formation of the vapor complexes. The CeO_2−ZrO_2 solid solutions are chlorinated in the presence of carbon. The resulting chlorides react with aluminum chloride to form the vapor complexes and are removed from the samples.

The apparatus used for the chemical filing process consisted of two tubular electric furnaces (furnaces A and B) and a fused silica reactor (Figure 1). The 0.30 g CeO_2−ZrO_2 solid solutions were mixed with 0−0.30 g of active carbon as a deoxidant, and the mixture was loaded on an alumina boat and introduced into furnace B. The anhydrous $AlCl_3$ (8.0×10^{-3} mol) powder in a glass ampule with a small hole was put into furnace A. After the temperature of the furnace B was raised to 1273 K in a N_2 flow, N_2−Cl_2 mixed gas (flow rate: N_2 = 30−600 mL/min, Cl_2 = 5 mL/min) was introduced into the reactor for 1−60 min. Then, N_2 gas with a flow rate of 300 mL/min was introduced for 1 h, and $AlCl_3$ was heated in furnace A at 363 K. The samples after the chemical filing were calcined in air at 673 K for 5 h for complete reoxidation and removal of excess carbon.

Three kinds of additional samples were prepared to confirm effects of chemical filing: the sample prepared by reoxidation of the oxa-CeO_2−ZrO_2 in air at 673 K for 5 h (reoxidized sample) and those prepared by heating of the oxa-CeO_2−ZrO_2 and the cp-CeO_2−ZrO_2 with active carbon in a N_2 flow at 1273 K for 1 h, followed by calcination in air at 673 K for 5 h.

Hydrogen consumption was evaluated by temperature-programmed reduction (TPR) experiments using a thermal conductivity detector of a gas chromatograph (Shimazu, GC-8A). To minimize the effects of adsorbed species on TPR, all of the samples were pretreated in He (80 mL min^{-1}) at 473 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

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1273 K (heating rate 10 K min^{-1}). The amount of hydrogen consumption was estimated from the integrated peak areas using CuO as a standard.

Ammonia TPD (temperature-programmed desorption) experiments were carried out to estimate the amount of acid sites on the samples by using the same thermal conductivity detector in the TPR experiment. Prior to TPD, 0.09 g of the samples was heated at 973 K for 1 h in a flow of He with a flow rate of 30 mL/min, then NH_3 (flow rate: 30 mL/min) was adsorbed on the samples at 373 K for 1 h, and the samples were treated again with He for 1 h at the same temperature. The TPD was performed under an He flow with a flow rate of 30 mL min^{-1} from room temperature to 973 K (heating rate 10 K min^{-1}).

The 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 (Jobin Yvon T64000). The spectra were excited with an Ar ion laser operating at 488.0 nm wavelength, and the laser power was 150 mW. BET surface area of the samples was measured with a Mircometrics FlowSorb II 2300 instrument. Bulk composition of the samples was determined by a X-ray fluorescent spectrometer (Rigaku System 3270A). The composition and electronic state of the surface of the samples were investigated by an X-ray photoelectron spectroscopy apparatus (Physical Electronics, model-5500MT). Microstructure of the powders was observed with a Hitachi H-800 transmission electron microscope operating at 200 kV.

Results and Discussions

Optimization of Chemical Filing Condition. In the chemical filing process, degree of chlorination determines surface and bulk properties of the samples. Desirable chemical filing condition can be obtained when surface chlorination is completed, and modification on bulk structure is minimized. Main factors that effect the chemical filing conditions are the amount of carbon and the N_2/Cl_2 ratio of the introduced gas.

Effects of the amount of active carbon were investigated by chlorination in a N_2-Cl_2 flow with the N_2/Cl_2 ratio of 6/1 for 1 h using 0, 0.06, 0.15, and 0.30 g of active carbon. When the amount of active carbon was 0 or 0.06 g, chlorination did not proceed. On the other hand, with 0.30 g of active carbon, it was found that the excess carbon inhibited the chlorination reaction. The same results have been reported for the chlorination of bastnaesite concentrate.[25] The optimal amount of active carbon is 0.15 g, which is half the mass of the starting material.

The effect of the N_2/Cl_2 ratio was investigated in the range of 6/1 to 120/1 by using the optimized amount of carbon. With the high Cl_2 content, the phase decomposition into CeO_2 and ZrO_2 occurred in a very short chlorination time, less than 5 min. This phase decomposition is rationalized as oxidation of Ce(III) in pyrochlore-type $Ce_2Zr_2O_7$, where chlorine acts on as a oxidizing agent. In the presence of carbon, Ce(III) is oxidized to form CeO_2, and a part of zirconium is chlorinated to form $ZrCl_4$.

$$Ce_2Zr_2O_7 + (^3/_2 - x)C + 2(2 - x)Cl_2 \rightarrow 2CeO_2 + xZrO_2 + (2 - x)ZrCl_4 + (^3/_2 - x)CO_2 \quad (2)$$

On the contrary, in the chemical filing condition with extremely low Cl_2 content, surface chlorination was not completed even after a long reaction time, more than 1 h. The N_2/Cl_2 ratio of 60/1 was found to be the most appropriate for complete chlorination of the surface.

Table 1. The Bulk and Surface Compositions of Oxa-CeO_2-ZrO_2 Powders after the Surface Treatment for Various Reaction Times

chlorin. time/min	comp. in bulk	comp. in surface
0[a]	$Ce_{0.4}Zr_{0.6}O_2$	$Ce_{0.45}Zr_{0.55}O_2$
5	$Ce_{0.4}Zr_{0.6}O_2$	$Ce_{0.47}Zr_{0.53}O_2$
10	$Ce_{0.4}Zr_{0.6}O_2$	$Ce_{0.53}Zr_{0.47}O_2$
50	$Ce_{0.4}Zr_{0.6}O_2$	$Ce_{0.74}Zr_{0.26}O_2$

[a] The calcined sample.

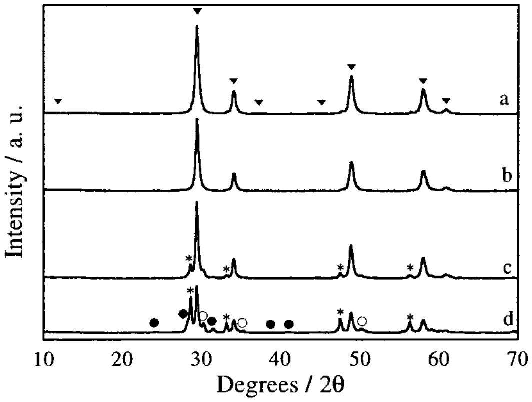

Figure 2. X-ray diffraction patterns of CeO_2-ZrO_2 solid solutions prepared from the oxalate, which are calcined (a) and chemical-filed for 5 (b), 10 (c), and 50 min (d): (▼) pyrochlore-like phase; (*) CeO_2; (●) monoclinic ZrO_2; and (○) tetragonal ZrO_2.

Structural Modification by Chemical Filing. Table 1 summarizes the surface and bulk composition of oxa-CeO_2-ZrO_2 powders after the surface treatment, which were determined by X-ray photoelectron spectroscopy (XPS) and X-ray fluorometry, respectively. The chlorination was carried out for 5, 10, and 50 min at $N_2/Cl_2 = 60/1$. X-ray fluorescence analysis showed that the CeO_2-ZrO_2 solutions contain only Ce and Zr. Because no trace of aluminum was detected, the possibility of the formation of Al_2O_3 by the reaction of samples with aluminum chloride can be excluded. It also should be mentioned that no peaks related to chlorine were observed in the XPS spectra, suggesting that no chloride or oxychloride species remained on the surface of the CeO_2-ZrO_2 solid solutions. Surface enrichment of cerium proceeded with increasing chlorination time, and the bulk composition of the samples was unchanged by the chemical filing treatment.

Figure 2 compares X-ray diffraction patterns of the oxa-CeO_2-ZrO_2 powders after the chemical filing treatment for various reaction times. As previously reported,[23] the CeO_2-ZrO_2 mixed oxide prepared from thermal decomposition of a cerium zirconyl oxalate had the cubic pyrochlore structure. Lattice contraction and formation of pyrochlore-like structure were observed after oxidation of the pyrochlore sample (Figure 2a). No apparent change of intensities or positions of the peaks was observed by the surface treatment with chlorine within 5 min (Figure 2b). After chlorination treatment for longer time, however, the XRD pattern indicated phase decomposition. The intensity of the peaks of the pyrochlore-like phase decreased, and new peaks of the

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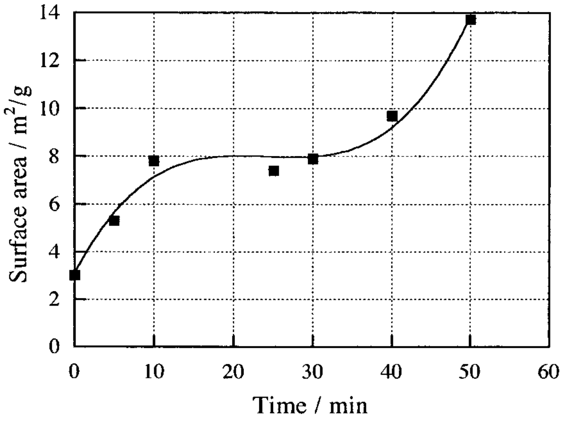

Figure 3. Relationship between the surface area of CeO_2-ZrO_2 solid solutions prepared from the oxalate and chlorination time in the chemical filing.

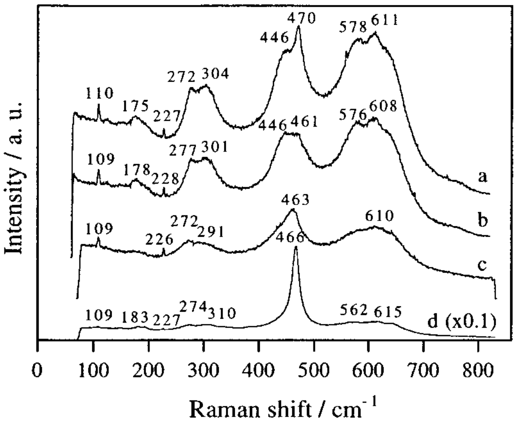

Figure 4. Raman spectra of CeO_2-ZrO_2 solid solutions prepared from oxalate, which are calcined (a) and chemical-filed for 5 (b), 10 (c), and 50 min (d).

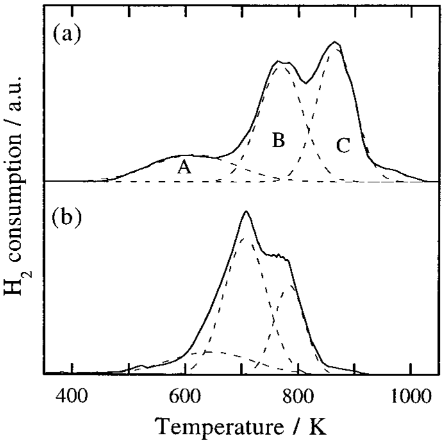

Figure 5. TPR profile of oxa-CeO_2-ZrO_2 solid solutions calcined (a) and chemical-filed for 5 min (b).

cubic CeO_2 phase and the monoclinic and tetragonal ZrO_2 phases appeared (Figure 2c,d).

The relationship between chlorination times and the surface areas of the samples in the chemical filing is shown in Figure 3. The surface area of the only reoxidized sample was 3.0 m^2/g, which was comparable to the value previously reported for the CeO_2-ZrO_2 powders prepared from a oxalate.[23] After the 5 and 10 min chlorination, the surface area increased to 5.3 and 7.8 m^2/g, respectively. After chlorination for 50 min, the surface area remarkably increased. From the results of the XRD investigations, the small and the large increases in the surface area are attributed to the modification on the surface and in the bulk structures of the samples, respectively.

Raman scattering is generally detectable within a depth of 10−100 nm from the surface of samples, whereas X-rays reach a depth of more than 1 μm from the surface. Therefore, Raman spectroscopy is more appropriate than X-ray diffraction for structural analysis of the surface of solids. Figure 4 shows Raman spectra of oxa-CeO_2-ZrO_2 solid solutions collected in the region 100−800 cm^{-1} with and without the chemical filing. For CeO_2-ZrO_2 solid solutions with a Ce/Zr ratio of about 1/1, there are three possible structures: tetragonal, fluorite, and pyrochlore-related.[26] The Raman spectrum of the reoxidized sample features six strong bands centered at 272, 304, 446, 470, 578, and 611 cm^{-1} and a shoulder band at about 640 cm^{-1}. This spectrum is similar to that of κ-phase, which is newly apparent because of the reduction and reoxidation of a solid-state-synthesized CeO_2-ZrO_2 (Ce/Zr = 1/1) solid solution.[17,18] In the pyrochlore structure $A_2B_2O_7$ (space group $Fd3m$), six Raman active modes $A_{1g} + E_g + 4\ T_{2g}$ have been predicted.[27] However, only four T_{2g} bands centered at 300−320, 395−400, 495−538, and 516−596 have been observed in the Raman spectra of $Ln_2Zr_2O_7$ (Ln = La, Nd, Sm, Gd) pyrochlore-type compounds.[27] Therefore, the peaks centered at 304, 470, and 578 in the Raman spectra of the reoxidized sample indicate the presence of the pyrochlore-like structure. The other three bands centered at 272, 446, and 611 are attributable to E_g bands of tetragonal solid solution. It seems that the structure of κ-phase is intermediate between tetragonal and pyrochlore by lowering of symmetry as a result of the displacement of oxygen from ideal positions.

After chlorination for 5 min, the T_{2g} band at 470 cm^{-1} decreases relative to the reoxidized sample, but the intensity of the other peaks remained unaltered. This suggests that oxygen displacement has occurred and the surface structure was distorted.

After chlorination for a longer time, the intensity of the bands attributed to the pyrochlore and tetragonal structures decreased, and a new band, which belongs to T_{2g} Raman active mode of fluorite structure, appeared at 463 cm^{-1}. This suggests that the high content of fluorite CeO_2 on the surface of the samples chlorinated for a long time is a result of the phase decomposition.

Effect of Chemical Filing on Oxygen Release Property. TPR profiles of the reoxidized and the chemical filed oxa-CeO_2-ZrO_2 powders are reported in Figure 5. Fornasiero et al.[10] reported that TPR profiles could be deconvoluted into several Gaussian-type profiles. The TPR profiles of the reoxidized and chemical-filed samples were deconvoluted into three Gaussians. Peak temperatures and hydrogen consumption of the deconvoluted peaks are described in Table 2. According to Fornasiero et al.,[28] the lowest-temperature peak is due to reduction both at the surface and in the bulk,

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Table 2. Peak Temperatures and H_2 Consumption in the TPR of Oxa-CeO_2-ZrO_2 Powders after the Chemical Filing for Various Reaction Time

	peak temp./K			H_2 consump./ ml g^{-1}			
chlorin. time/min	A	B	C	A	B	C	total
0[a]	615	768	865	7.9	14.3	15.4	37.6
5	645	706	784	8.9	17.1	8.7	34.7
10	622	715	795	8.0	17.9	4.6	30.5
30	622	703	781	6.9	11.3	6.9	25.1
50	669	725	816	10.8	6.8	4.8	22.4

[a] The calcined sample.

Table 3. Peak Temperatures and H_2 Consumption of the Recycled and Fresh Samples in the TPR for Oxa-CeO_2-ZrO_2 and Reduced/Reoxidized CeO_2-ZrO_2

sample	no. recycles	peak temp./K	H_2 consump./ ml g^{-1}
calcined	0	768	37.6
chemical-filed	0	707	34.7
	10	659	25.8
carbon-treated	0	751	26.3
	6	715	17.3
reduced/reoxidized	0	756	24.2
	10	784	23.4

because the amount of H_2 consumption calculated from the linear relationship with surface area[29] is much lower than that estimated experimentally for the lowest-temperature peak. Therefore, the first peak in the TPR profiles corresponds to the reduction of the surface and bulk, and both of the second and the third peaks are attributed to reduction processes in the bulk. This splitting of the reduction process in the bulk into the three peaks is a characteristic of a CeO_2-ZrO_2 solid solution prepared using an oxalate precursor,[23] and it suggests the existence of three kinds of environments around oxygen atoms in the lattice. Although the peak temperature for the first peak was not largely altered by the chemical filing process, those of the second and the third peaks were lowered by more than 50 K. The correlation between low-temperature reduction peaks in the TPR profiles and three-way activity has been established for the CeO_2-based catalysts.[30,31] The disappearance of low-temperature peaks in TPR spectra causes a significant deactivation of the catalysis. For example, the conversions of carbon monoxide and nitrogen monoxide at the stoichiometric A/F ratio decreased greatly together from ca. 80% to ca. 60%.[31] In addition, the oxygen release property at low temperatures also plays an important role in the reduction of hydrocarbon emission after cold starts. Recently, Zamar et al. measured activity of CeO_2-based solid solutions for methane combustion.[32] In their work, the TPR peak temperatures of $Ce_{0.8}Zr_{0.2}O_2$ and $Ce_{0.8}Hf_{0.2}O_2$ with similar surface areas were about 820 and 870 K, respectively, and methane conversion in 820 K over the former was about 8% higher than that over the latter, suggesting that the lowering in oxygen release temperature by 50 K improves the activity of hydrocarbon combustion.[32] The H_2 consumption for the third peak decreased, suggesting that the release of relatively stable oxygen became difficult because of the annealing at high temperatures during the chemical filing treatment.

Total H_2 consumption gradually decreased with increasing chlorination time from 5 to 50 min. This decrease is partially correlated to the decrease in the component of pyrochlore-like structure by the phase separation to CeO_2 and ZrO_2. Another reason is the surface Ce enrichment shown by the XPS measurements. Dissociation of H_2 over the ZrO_2 surface occurred at lower temperatures compared to that over the CeO_2 surface, and surface sites of strong Lewis acidity, which may play a role in H_2 activation, are generated by heat treatment of ZrO_2.[10] Consequently, the lower the zirconium content in the surface of CeO_2-ZrO_2 solid solution, the lower the Lewis acidity and the surface activity against H_2 dissociation. Actually, the amount of desorbed NH_3 of the chemical-filed sample in the NH_3 TPD experiments was smaller than that of the reoxidized sample, indicating the decrease in Lewis acidity.

The chemical filing treatment was most successful with chlorination for 5 min because of the largest H_2 consumption at low temperatures. The reproducibility of this result was confirmed by the profiles of the three TPR runs of the samples independently treated with the same optimized condition.

Mechanism of the Chemical Filing Process. The oxygen release property was also investigated for the reduced/reoxidized CeO_2-ZrO_2 powders with and without the chemical filing treatment by means of the TPR techniques. Only a single peak was observed for the both TPR profiles in contrast to those of the oxa-CeO_2-ZrO_2 powders. The H_2 consumption of the sample increased from 24.2 to 29.3 mL g^{-1} by the chemical filing treatment. However, the peak temperature of the sample did not change from 750 K after the chemical filing. The similar result was also obtained in the case of the cp-CeO_2-ZrO_2 powders. These minor improvements in the reduction behavior of the reduced/reoxidized and the cp-CeO_2-ZrO_2 powders by the chemical filing process indicate that the process has a significant effect on the oxygen release property only to the oxa-CeO_2-ZrO_2 powder.

There still remains the possibility that the improvement of the oxa-CeO_2-ZrO_2 powder in oxygen release property by the chemical filing is simply ascribed to the reducing action of carbon, because the reduction/reoxidation cycle generally lowers the oxygen release temperature of CeO_2-ZrO_2 solid solutions. Then, the reduction behavior of the oxa-CeO_2-ZrO_2 powder prepared by heating with active carbon and subsequent reoxidization was investigated and compared with those of the reoxidized and the chemical-filed samples for confirmation of the chemical filing effect. The peak temperatures and H_2 consumption in TPR profiles for these samples are summarized in Table 3. Peak temperature for the carbon-treated sample was lower only by 20 K than that for the calcined one, and the H_2 consumption was significantly lowered by carbon treatment, to 26.3 mL g^{-1}. This indicates that the effect of carbon reduction on the oxygen release property of the oxa-CeO_2-ZrO_2 sample is smaller than that of the chemical filing.

Figure 6 shows transmission electron micrographs of the reoxidized and the chemical-filed oxa-CeO_2-ZrO_2

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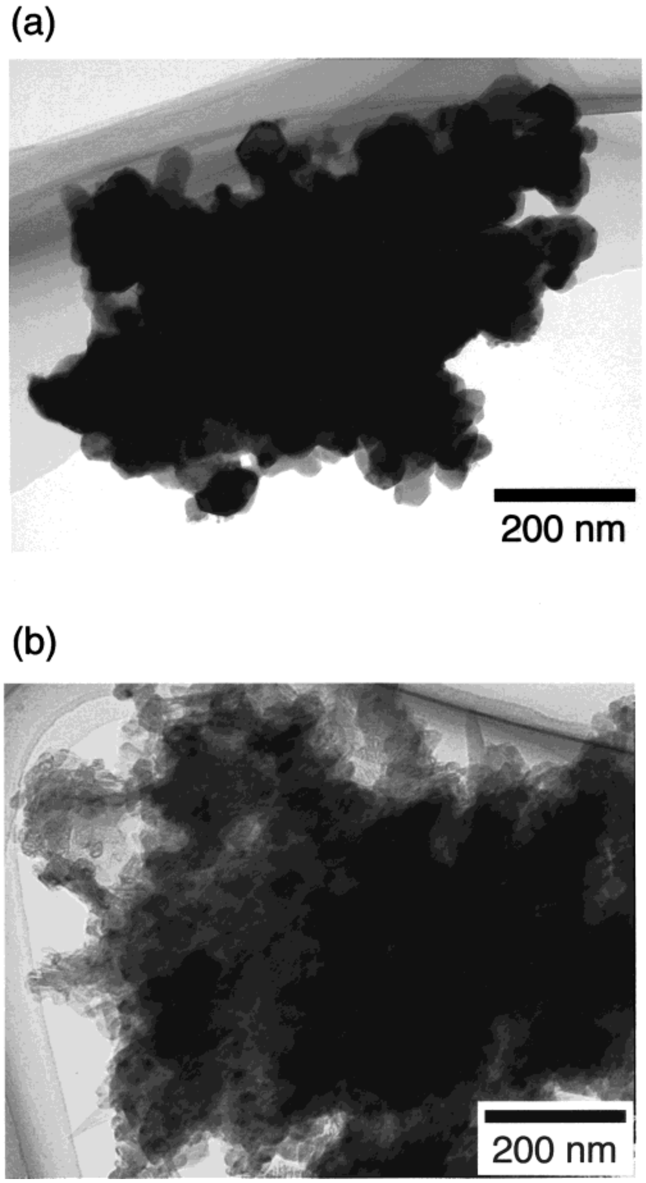

Figure 6. Transmission electron micrograph of CeO_2-ZrO_2 solid solutions prepared from the oxalate, which are calcined (a) and chemical-filed for 5 min (b).

powders. Surface morphology of the chemical filed powder was considerably different from that of the calcined one: whereas the surface of the reoxidized sample was almost smooth, that of the chemical-filed sample was very rough. These TEM observations are consistent with the surface structural modification suggested by the Raman spectra and the XPS measurements. This modification is induced by oxidative chlorination with Cl_2. Through chlorination, Ce^{3+} is oxidized to Ce^{4+} and zirconium is partially removed to form volatile $ZrCl_4$. As a result, defective structure formed on the surface. This defective surface phase facilitates the diffusion of the bulk oxygen into the surface, resulting in the improvement in the oxygen release properties. Because the existence of Ce^{3+} in the lattice is important to proceed with the chlorination, the cp-CeO_2-ZrO_2 powder in which only Ce^{4+} exists is hard to make undergo the chemical filing. The proposed mechanism of the chemical filing is illustrated in Figure 7.

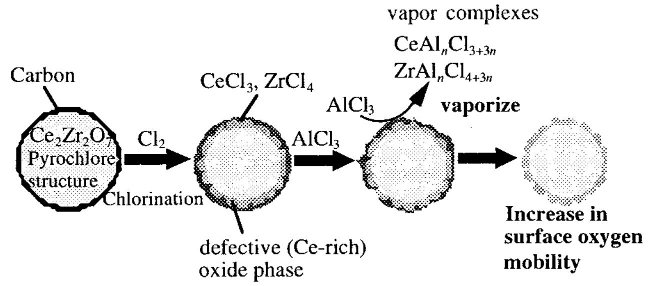

Figure 7. Schematic mechanism proposed for surface modification by the chemical filing process.

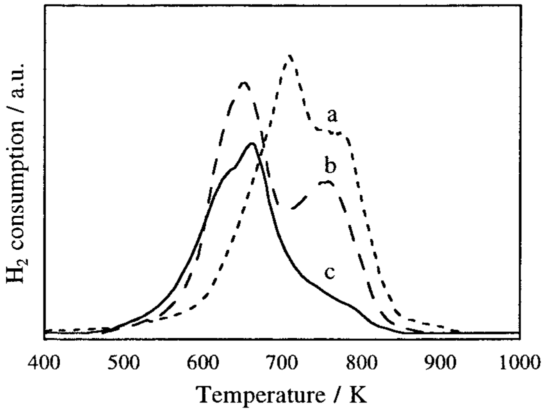

Figure 8. TPR profile of the CeO_2-ZrO_2 powders prepared from the oxalate, which are chemical-filed (a) and recycled 1 (b) and 10 (c) times after the chemical filing.

Reduction−Oxidation Behavior and Thermostability of CeO_2-ZrO_2 Powders. The effect of continuous reduction and reoxidation cycles on the structure and reduction behavior was investigated for the CeO_2-ZrO_2 powders. The reduction was carried out in a flow of H_2 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 He for 15 min, the sample was reoxidized in a flow of air for 10 min at 1273 K. The TPR profiles of the chemical-filed oxa-CeO_2-ZrO_2 powders after the reduction and reoxidation cycles for 1 and 10 times are compared in Figure 8. The H_2 consumption and peak temperatures in the TPR of the cycled and fresh samples for the chemical-filed and the carbon-treated oxa-CeO_2-ZrO_2 and the reduced/reoxidized CeO_2-ZrO_2 are summarized in Table 3. The peak temperature in the TPR of the chemical-filed sample was further lowered by the one reduction/reoxidation cycle by more than 50 K, and the amount of H_2 consumption slightly decreased. After 10 reduction/reoxidation cycles, the peak temperature remain unaltered, although the H_2 consumption decreased. The TPR profiles after 20 and 30 cycles were comparable to that after 10 cycles. This decrease in H_2 consumption is mainly due to the disappearance of the higher temperature peak, and H_2 consumption at the lower temperature peak was almost unaltered even after 30 cycles. The similar tendency was observed in the case of the carbon-treated sample. After 6 cycles, the peak at high-temperature disappeared, and the peak temperature decreased from 751 to 715 K. However, this temperature is still more than 50 K higher than that of the 30-cycle, chemical-filed sample, suggesting that the chemical-filed sample shows a higher oxygen release

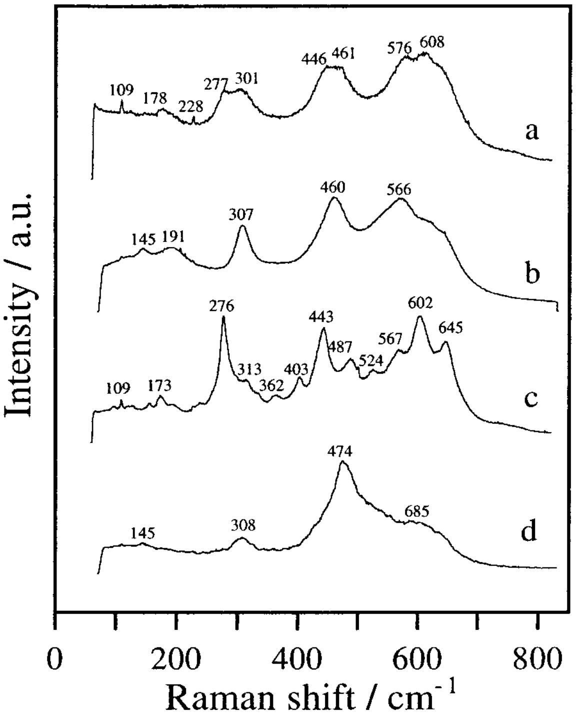

Figure 9. Raman spectra of chemical-filed CeO_2-ZrO_2 solid solutions, which are fresh (a) and recycled 10 times (b), and reduced/reoxidized CeO_2-ZrO_2 solid solutions, which are fresh (c) and recycled 6 times (d).

property than the carbon-treated sample even after the redox cycles at high temperatures. The improvement in the oxygen release property by the reduction/reoxidation cycles was explained on the basis of formation of mesoporosity, which should be attributed to the stress and the coalescence of dislocations induced by the large expansion/shrinkage of the lattice.[10] By extensive sintering during this treatment, however, surface area of the sample decreased. The TPR profile of the cycled reduced/reoxidized sample features the shift of peak temperatures to about 50 K higher compared to the fresh one. Sintering and phase transition by high-temperature redox processes are the main possible causes of the increase in the oxygen release temperature.

The Raman spectra of the chemical-filed sample and the reduced/reoxidized CeO_2-ZrO_2 sample after the reduction/reoxidation cycles are shown in Figure 9. The Raman spectra of the recycled chemical-filed sample is somewhat different from that of the fresh sample. The three E_g bands of tetragonal structure at 272, 446, and 640 cm^{-1} disappeared, and only the bands attributed to pyrochlore-like structure remained. This agrees with the decrease in the number of peaks in the TPR profile, suggesting that the high-temperature redox cycles induce the homogenization of the solid solution. This phenomenon seems to be common for the CeO_2-ZrO_2 powders derived from oxalate, because the similar behavior was also observed for the carbon-treated sample. On the other hand, the Raman spectra of the reduced/reoxidized sample was greatly changed by the reduction/reoxidation cycles. Many bands related to the pyrochlore-like structure in the fresh sample disappeared, and strong broad band centered at 474 cm^{-1} with a shoulder at 685 cm^{-1} and two weak bands at 145 and 308 cm^{-1} appeared. The peak at 474 cm^{-1} suggests the presence of a fluorite phase,[10] and the other peaks are attributed to the tetragonal phase. These results show that large structural modification with phase transition occurred during the redox cycles.

Durability of the samples was also investigated in the oxidizing atmosphere at high temperature. The reduction behavior of the chemical-filed CeO_2-ZrO_2 powders calcined in a flow of air at 1323 K for 5 h was also evaluated by the TPR. Although the amount of H_2 consumed in the TPR was comparable to that for the 30-cycle sample, the peak temperature was lower by about 20 K than that of the fresh sample. In contrast, the peak temperature of the reduced/reoxidized CeO_2-ZrO_2 increased by about 30 K after the oxidation, and the H_2 consumption also decreased. This indicates that the thermostability of the chemical filed sample is superior to those of the samples prepared by the conventional methods. The oxygen release temperature of the chemical-filed sample after high-temperature oxidation is still lower than that of the fresh reduced/reoxidized sample.

Conclusion

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 process was only effective for the CeO_2-ZrO_2 powder prepared by thermal decomposition of oxalate, because the filing proceeded by oxidative chlorination with chlorine, which accompanied oxidation of Ce^{3+} and the removal of Zr. The results of TEM observation and Raman spectra showed the surface modification of the solid solution by the filing process. The oxygen release temperature of the chemical-filed sample was more than 50 K lower than that of the sample without filing. The amount of the released oxygen was nevertheless unchanged by the treatment. It was confirmed by the experiments using the blank sample that the improvement in oxygen release property was not attributed to the reduction with carbon but to the chemical filing effect. The repetitive reduction/reoxidation cycles further lowered the reduction temperature of the chemical-filed solid solution, and the reduction temperature was maintained after 30 redox cycles. The oxygen release property of the sample after oxidation at 1323 K for 5 h was superior to that of the solid solution prepared by several conventional methods, suggesting that the chemical filing improves not only reduction behavior but also durability of CeO_2-ZrO_2 solid solutions.

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