Characteristics in oxygen storage capacity of ceria–zirconia mixed oxides prepared by continuous hydrothermal synthesis in supercritical water

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Abstract
Continuous hydrothermal synthesis in supercritical water (supercritical synthesis) is a method to prepare metal oxide nanoparticles rapidly and continuously using supercritical water. Highly crystallized nanoparticles of homogeneous complex metal oxides as well as single metal oxides could be produced easily by the supercritical synthesis. Ceria–zirconia mixed oxide is widely used as oxygen storage material, for example, in the three-way catalysts for the clean up of automotive gases. Ceria–zirconia mixed oxides were prepared by the new supercritical synthesis method and also by the conventional co-precipitation method. The characteristics in oxygen storage capacity (OSC) of ceria–zirconia mixed oxide prepared by the supercritical synthesis were compared with those by the co-precipitation method. It was confirmed through physical characterizations with N2 adsorption, SEM, TPR and O2-uptake that the supercritical synthesis could lead to ceria–zirconia mixed oxides with higher thermal stability and better OSC due to its morphology.
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Keywords: Ceria–zirconia mixed oxide; Co-precipitation; Hydrothermal synthesis; Supercritical water; Oxygen storage capacity (OSC); Thermal stability

1. Introduction
Continuous hydrothermal synthesis in supercritical water (supercritical synthesis) is a method to prepare metal oxide nanoparticles using supercritical water as antisolvent. The dielectric constant of water decreases with increasing temperature at a given pressure. Inorganic salts (e.g. NaCl) which are soluble at room temperature become insoluble in supercritical water and precipitate from solution. In case of heavy metals, hydrated metal ions are hydrolyzed and proceed to precipitate as crystalline metal oxides through dehydration at a high temperature. This is the principal mechanism of metal oxide formation by hydrothermal synthesis. When the solution of metal precursors was mixed with supercritical water and heated rapidly, metal oxide nanoparticles could be produced rapidly and continuously by fast hydrolysis and dehydration reaction. Highly crystallized nanoparticles of homogeneous complex metal oxides as well as single metal oxides could be produced easily by the supercritical synthesis. Also the size and the morphology of metal oxide particles could be controlled easily by changing temperature and pressure of supercritical water [1,2].

The three-way catalysts are widely used to control the automotive gases. The CeO2-based materials act as an oxygen buffer for the three-way catalysts by releasing and uptaking oxygen through redox processes by the Ce4+/Ce3+ couple (CeO2 $\rightarrow$ CeO2–x + x/2O2), and increase the efficiency of the catalysts by enlarging the air-to-fuel operating window. Since the mid 1990s, ceria–zirconia mixed oxides have been chosen as a real alternative of ceria in the formulation of the three-way catalysts due to their enhanced stability against thermal sintering as well as improved redox properties [3–5].

In this work, ceria–zirconia mixed oxides were prepared by a new synthesis method (continuous hydrothermal synthesis in supercritical water) and also by a conventional synthesis method (co-precipitation). Physical property, redox property and thermal stability of ceria–zirconia mixed oxides prepared by supercritical synthesis were compared with those prepared by co-precipitation method.

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2. Experimental

The ceria–zirconia mixed oxides (Ce$_x$Zr$_{1-x}$O$_2$ (sc/fresh), $x$ = 1, 0.65, 0.5, 0.2, 0) were prepared by the supercritical synthesis method, and the schematic diagram for the synthesis apparatus is shown in Fig. 1. The synthesis process can be outlined as in the following. Distilled water, pumped into the system using a high pressure pump, was heated to a moderate temperature by heat exchanger and heated further to a desired temperature by preheater. The solution of metal precursors (Zr(NO$_3$)$_2$, Ce(NO$_3$)$_3$) and ammonia water for pH control, pumped into the system using high pressure pumps, were mixed with supercritical water at the mixing point located above the reactor. The sufficient reaction time for the formation of ceria–zirconia mixed oxide nanoparticle was provided by the reactor to maintain supercritical condition. The synthesized ceria–zirconia mixed oxide was collected by filter, and followed by spray drying to obtain the final product.

A conventional co-precipitation method was also applied to obtain ceria–zirconia mixed oxides (Ce$_x$Zr$_{1-x}$O$_2$ (cop/fresh),...
The solution of metal precursors was prepared from ZrO(NO$_3$)$_2$ and Ce(NO$_3$)$_3$. Hydroxide was precipitated by adding the solution of metal precursors dropwise to ammonia water (2 wt%) at 30°C. The pH of the solution was kept at 10.2. The hydroxide was filtered, washed, and dried in a convection oven at 100°C for 12 h. Finally, ceria–zirconia mixed oxide was obtained by calcining the hydroxide in air flow at 700°C for 5 h.

BET surface area, pore volume and pore size distribution of ceria–zirconia mixed oxides were measured by N$_2$ adsorption using ASAP2010 (Micromeritics Inc.). The samples were degassed at 150°C, and N$_2$ adsorption was carried out at 77 K.

The crystal structures of ceria–zirconia mixed oxides were confirmed by powder X-ray diffraction (XRD) pattern using monochromic Cu K$\alpha$ radiation (Rigaku, D/MAX III). The average crystallite size was also measured by the X-ray line broadening technique employing the Scherrer formula using the profiles of the (1 1 1) peak.

SEM images of ceria–zirconia mixed oxides were obtained by a Phillips SEM-535M microscope operating at an acceleration voltage of 20 kV. The samples were prepared by sprinkling the powder oxides onto double-sided sticky tape and mounted on a microscope stub. The samples were coated with gold sputtered.

Temperature-programmed reduction (TPR) for the ceria–zirconia mixed oxide was carried out in a conventional flow apparatus (Pulsechemisorb 2705, Micromeritics Inc.). A 0.05 g of sample was pretreated in the O$_2$ (5%)/He flow at 550°C for 1 h, and cooled in the He flow from 150°C to room temperature for O$_2$ purge. The sample was then reduced in the H$_2$(5%)/Ar flow with the temperature increasing from room temperature to 1000°C at a constant heating rate of 10°C/min. The 4A molecular sieve trap was used to eliminate the produced H$_2$O during reduction, and the amount of consumed H$_2$ was detected using thermal conductivity detector (TCD).

Total oxygen storage capacity (OSC) of prepared ceria–zirconia mixed oxide, the total amount of O$_2$ which may be extracted from the sample at a pre-established temperature and partial pressure of the reducing agent (H$_2$, CO, etc.), was measured.

Table 1
Oxygen uptake at 427°C of prepared ceria–zirconia mixed oxides

<table>
<thead>
<tr>
<th></th>
<th>(sc/fresh)</th>
<th>Total OSC (µmol-O$_2$/g)</th>
<th>(cop/fresh)</th>
<th>Total OSC (µmol-O$_2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>533</td>
<td>CeO$_2$</td>
<td>533</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.65}$Zr$</em>{0.35}$O$_2$</td>
<td>680</td>
<td>Ce$<em>{0.65}$Zr$</em>{0.35}$O$_2$</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>629</td>
<td>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.25}$Zr$</em>{0.75}$O$_2$</td>
<td>270</td>
<td>Ce$<em>{0.25}$Zr$</em>{0.75}$O$_2$</td>
<td>429</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0</td>
<td>ZrO$_2$</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
BET surface area, pore volume, crystallite size and total OSC of pure CeO$_2$ and Ce$_{0.65}$Zr$_{0.35}$O$_2$ before and after redox aging at 1000°C

<table>
<thead>
<tr>
<th></th>
<th>CeO$_2$ (sc)</th>
<th>CeO$_2$ (cop)</th>
<th>Ce$<em>{0.65}$Zr$</em>{0.35}$O$_2$ (sc)</th>
<th>Ce$<em>{0.65}$Zr$</em>{0.35}$O$_2$ (cop)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>Fresh</td>
<td>Fresh</td>
<td>Fresh</td>
<td>Fresh</td>
</tr>
<tr>
<td>Aged</td>
<td>Aged</td>
<td>Aged</td>
<td>Aged</td>
<td>Aged</td>
</tr>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>52.78</td>
<td>0.86</td>
<td>38.56</td>
<td>0.97</td>
</tr>
<tr>
<td>Pore volume (cm$^3$/g)</td>
<td>0.207</td>
<td>0.008</td>
<td>0.142</td>
<td>0.002</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>16.2</td>
<td>96.1</td>
<td>15.8</td>
<td>90.4</td>
</tr>
<tr>
<td>Total OSC (µmol-O$_2$/g)</td>
<td>530</td>
<td>380</td>
<td>530</td>
<td>360</td>
</tr>
</tbody>
</table>

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$\text{x} = 1, 0.65, 0.5, 0.25, 0)$. The solution of metal precursors was prepared from Zr(NO$_3$)$_2$ and Ce(NO$_3$)$_3$. Hydroxide was precipitated by adding the solution of metal precursors dropwise to ammonia water (2 wt%) at 30°C. The pH of the solution was kept at 10.2. The hydroxide was filtered, washed, and dried in a convection oven at 100°C for 12 h. Finally, ceria–zirconia mixed oxide was obtained by calcining the hydroxide in air flow at 700°C for 5 h.

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Total oxygen storage capacity (OSC) of prepared ceria–zirconia mixed oxide, the total amount of O$_2$ which may be extracted from the sample at a pre-established temperature and partial pressure of the reducing agent (H$_2$, CO, etc.), was measured.
determined by the O\textsubscript{2}-uptake. The O\textsubscript{2}-uptake of the ceria–zirconia mixed oxide was carried out in the same apparatus as that of TPR. The sample was reduced in the H\textsubscript{2}(5%)/Ar flow at 1000 °C for 30 min, and cooled to 427 °C. An oxygen pulse was injected every 3 min to the sample in the main stream of He at 427 °C to obtain the breakthrough curve, from which the total OSC was determined.

The thermal stability of prepared ceria–zirconia mixed oxide could be evaluated by comparing the properties of the sample redox-aged at high temperature with those of the fresh sample. In a conventional flow apparatus, ceria–zirconia mixed oxide was reduced in the H\textsubscript{2}(5%)/He flow at 1000 °C for 6 h, and oxidized in the O\textsubscript{2}(5%)/He flow at 1000 °C for 6 h. The redox-aged samples prepared by the supercritical synthesis were denoted as “sc/aged”, and those by the co-precipitation as “cop/aged”.

3. Results and discussion

The XRD patterns of ceria–zirconia mixed oxides prepared by the supercritical synthesis and the co-precipitation are shown in Fig. 2. The fresh oxides prepared by the supercritical synthesis were denoted as “sc/fresh”, and those by the co-precipitation as “cop/fresh”. It could be confirmed from the XRD patterns that ceria and ceria–zirconia mixed oxides prepared by two synthesis methods had the same crystal structure as pure ceria, and prepared zirconia had the same crystal structure as pure zirconia. In case of both synthesis methods, the characteristic peak of ceria is progressively shifted to larger angles as the Zr content increases. This is due to a contraction of lattice cell parameter by insertion of ZrO\textsubscript{2} into CeO\textsubscript{2} fluorite lattice.

The results of temperature-programmed reduction (TPR) of ceria–zirconia mixed oxides prepared by the supercritical synthesis and the co-precipitation are shown in Fig. 3. In case of all samples prepared by two synthesis methods, the addition of Zr to CeO\textsubscript{2} resulted in shifting the reduction peak to a lower temperature below 800 °C. It was reported that this reduction peak around 800 °C are due to the reduction of bulk oxides [6,7]. The intensity of the bulk oxide reduction peaks decreased with the Zr content of the sample, and pure ZrO\textsubscript{2} was not reduced by H\textsubscript{2}. The reduction characteristics of the samples at high temperature (>800 °C) were mutually similar. On the other hand, the characteristic peak at a low temperature (500–550 °C) are due to the reduction of surface oxides [6,7] which are more prominent in the samples prepared by the co-precipitation method rather than by the supercritical synthesis. The ceria–zirconia fresh samples prepared by the supercritical synthesis do not seem to be in a better position in view of reducibility. For their practical application, as oxygen storage...
materials, for example, in the three-way catalysts, the ceria–zirconia materials are exposed to severe redox conditions at very high temperatures (>1000 °C) and lose their redox properties easily.

The O2-uptakes at 427 °C of ceria–zirconia mixed oxides prepared by the supercritical synthesis and the co-precipitation method are shown in Table 1. The total OSC of fresh Ce0.65Zr0.35O2 was the highest among the samples prepared by each synthesis method. The total OSC of Ce0.65Zr0.35O2 (sc/fresh) and Ce0.65Zr0.35O2 (cop/fresh) were 680 and 700 μmol-O2/g, respectively. The fresh ceria–zirconia mixed oxides prepared by the co-precipitation method had a higher total OSC than those by the supercritical synthesis, and the total OSC of pure ZrO2 was zero regardless of the synthesis methods. The TPR and the O2-uptakes are in good correlation as expected.

BET surface area, pore volume, crystallite size and total OSC of pure CeO2 and also Ce0.65Zr0.35O2 which had the highest total OSC among the prepared ceria–zirconia mixed oxides were compared before and after redox-aging as shown in Table 2, and the XRD patterns and TPR results are shown in Figs. 4 and 5, respectively. The redox-aged samples prepared by the supercritical synthesis were denoted as “sc/aged”, and those by the co-precipitation as “cop/aged”. It could be confirmed from the XRD patterns that pure CeO2 and also Ce0.65Zr0.35O2 prepared by two synthesis methods kept their crystal structure after redox-aging, while their characteristic peak became narrower and higher due to particle-sintering during redox-aging.

It can be seen from the TPR spectra that the characteristic peak of pure CeO2 prepared by the co-precipitation method near 500 °C due to surface reduction of the fresh sample disappeared after redox-aging. The pore volume decreased from 0.142 to 0.002 cm3/g and the surface area decreased greatly from 38.56 to 0.97 m2/g. The crystallite size also

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Fig. 5. TPR results of (a and b) pure CeO2 and (c and d) Ce0.65Zr0.35O2 before and after redox-aging: (a1) CeO2 (cop/fresh), (a2) CeO2 (cop/aged); (b1) CeO2 (sc/fresh), (b2) CeO2 (sc/aged); (c1) Ce0.65Zr0.35O2 (cop/fresh), (c2) Ce0.65Zr0.35O2 (cop/aged); (d1) Ce0.65Zr0.35O2 (sc/fresh), (d2) Ce0.65Zr0.35O2 (sc/aged).
increased from 15.8 to 90.4 nm. The pores of the sample must be collapsed by particle-sintering during redox-aging at 1000 °C [8]. Additionally, the total OSC also decreased from 530 to 360 μmol-O_2/g.

Pure CeO_2 prepared by the supercritical synthesis underwent the similar changes to that by the co-precipitation method. The pore volume of the sample decreased greatly from 0.207 to 0.008 cm³/g and the surface area decreased greatly from 52.78 to 0.86 m²/g. Additionally, the crystallite size increased from 16.2 to 96.1 nm and the total OSC decreased from 530 to 380 μmol-O_2/g. Pure CeO_2 were not thermally stable in any case.

Two reduction peaks also appeared near 550 and 800 °C in the TPR spectra of Ce_{0.65}Zr_{0.35}O_2 (cop/fresh) prepared by the co-precipitation method. Like pure CeO_2, it was deduced that they were originated by surface reduction and bulk reduction of the sample, respectively. For redox-aged sample, however, only one large reduction peak was observed near 670 °C. It implies that the bulk reduction of the redox-aged sample occurred at a rather moderate temperature while the role of surface reduction diminished. The lattice oxygen should have migrated more easily in the bulk after redox-aging [9]. But like pure CeO_2, the pore volume and surface area after redox-aging decreased from 0.070 to 0.021 cm³/g, and from 55.22 to 3.78 m²/g, respectively. The crystallite size also increased from 7.8 to 12.8 nm and total OSC decreased from 700 to 330 μmol-O_2/g.

The Ce_{0.65}Zr_{0.35}O_2 (sc/aged) showed in its TPR spectra one large reduction peak near 575 °C, which is lower than that by the co-precipitation method. As in the sample prepared by co-precipitation method, the bulk reduction must be dominant due to redox-aging while the role of surface reduction diminished. The shift of the reduction peak toward lower temperature indicates that the supercritical synthesis can provide the ceria–zirconia mixed oxides with better reduction properties especially through redox-aging treatment. Accordingly, it could be inferred that the lattice oxygen in the mixed oxide prepared by the supercritical synthesis could migrate more easily than that by the co-precipitation method after redox-aging. The pore volume before and after redox-aging were 0.303 and 0.159 cm³/g, the surface area were 94.30 and 20.14 m²/g, the crystallite size were 6.8 and 21.1 nm, and the total OSC before and after redox-aging were 680 and 600 μmol-O_2/g, respectively. These changes before and after redox-aging can be a measure of thermal stability. It could be assured that Ce_0.65Zr_0.35O_2 prepared by the supercritical synthesis method in supercritical water had a higher thermal stability than that by the co-precipitation method.

The SEM images and pore size distributions of Ce_{0.65}Zr_{0.35}O_2 before and after redox-aging are shown in Figs. 6 and 7, respectively. The pores seemed to be created from ceria–zirconia mixed oxide nanoparticles when they were agglomerated, and the interstitial space between nanoparticles in the agglomeration might act as pores. In case of the supercritical synthesis, a lot of metal oxide nanoparticles might be precipitated very fast and the precipitated nanoparticles...
could be agglomerated rather coarsely. The sparsely agglomerated morphology, such as the SEM image of Fig. 6a, could be expected in supercritical synthesis. In case of the co-precipitation method, precipitation and agglomeration of metal oxide nanoparticles could occur simultaneously and the precipitated nanoparticles could interact with each other. Accordingly the densely agglomerated morphology could be obtained in co-precipitation as in the SEM image of Fig. 6b. The pores with a diameter larger than 10 nm observed in the fresh mixed oxide prepared by the supercritical synthesis rather increased to near 30 nm after redox-aging, while the sparsely aggregated morphology was almost retained (Figs. 6a and 7a). On the other hand, the small pores less than 5 nm and the densely aggregated morphology observed in the fresh mixed oxide prepared by the co-precipitation method were easily collapsed almost to complete sintering by redox-aging (Fig. 6b and 7b). It could be suggested that the densely aggregated morphology in the ceria–zirconia mixed oxide prepared by the co-precipitation method could prevent the lattice oxygen from migrating from the bulk to the atmosphere, leading to poor reduction and thermal property compared to those by the supercritical synthesis.

4. Conclusion

Ceria–zirconia mixed oxide is an important component as oxygen storage material, for example, in the three-way catalysts. The continuous hydrothermal synthesis in supercritical water was used as a new synthesis method to obtain ceria–zirconia mixed oxide with better OSC properties. This method has an advantage that highly crystallized nanoparticles of homogeneous complex metal oxide as well as single metal oxide could be produced easily and rapidly. The OSC characteristics of ceria–zirconia mixed oxide prepared by the continuous hydrothermal synthesis in supercritical water were compared with those by the conventional co-precipitation method. It was confirmed through physical characterizations with N₂ adsorption, SEM, TPR and O₂-uptake that the continuous hydrothermal synthesis in supercritical water could lead to ceria–zirconia mixed oxides with higher thermal stability and better OSC due to its morphology.

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