Store and Release of Oxygen of Ceria–Zirconia Solid Solution Synthesized by Solid Phase Reaction at Near Room Temperature

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Capability of oxygen store and release of ceria–zirconia solid solution made by attrition mill process was measured by thermo-gravimeter with 1mass% of Pt. Ceria–zirconia solid solution made by conventional heating method of ceria powder with zirconium salt was also characterized for comparison. Capability of oxygen store and release of ceria–zirconia solid solution made by attrition mill process is about three times larger than that of conventionally made samples. And, the point, where zirconium content is 100% on the relation between capability of oxygen store and release and zirconia content in the ceria–zirconia solid solution, corresponds to the state in which the valence of all the cerium ion being contained in the solid solution is 3. This fact suggests that the mechanism, that the increase of capability of oxygen store and release by dissolving zirconia into ceria, is that cerium ions, which are smaller than cerium ions of the valence 4, release the strain caused by the expansion due to a reduction of cerium ions.

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1. Introduction

Catalytic system is used for cleaning exhaust gas from an automobile, in which noble metal catalyst, mainly platinum, and auxiliary catalysts are installed. The activity of the catalysts reaches their maximum, when the exhaust gas is nearly neutral, or oxydic components such as NO and molecular oxygen, and reductive components such as HC, H2, and CO, are nearly absent. In driving an automobile, more fuel is supplied to the engine in accelerating period, and less fuel in cruising as well as decelerating, accordingly HC, H2, and CO rich exhaust gas or oxygen and NO rich exhaust gas is resulted, alternatively.1,2) So averaging the composition of the exhaust gas over the accelerating and decelerating periods is needed in the catalytic system for more complete cleaning, by storing oxygen in acceleration period and releasing oxygen in cruising or deceleration period. For that, some material capable of store and release of oxygen is necessary for the system. Such material would be effective also to increase activity of the system by giving oxygen to the reaction of oxidation and remove oxygen from reducing reaction, besides averaging the composition.1,2,3,4)

Oxygen store in a solid means the increase of valence of the cation composing the material, and the release means the decrease. So the material must be composed of valence-variable cations and oxygen.

There are so many oxides composed of valence-variable elements, such as copper-oxides, ferrous oxides, chromia, ceria, and so on. Some of the oxides are reduced to metals, causing a large volume change, which results crumbling of the material. These materials cannot be applied to the system. Cerium ion has the valence of 4 in its pure oxide (CeO2), and occasionally has that of 3 in compound oxides in which other cations are present as the component. This means the valence change of cerium ion would be enhanced through coexistence with other cations. Furthermore cerium oxides cannot be reduced to metal, and the volume change in the process CeO2–Ce3+O3¨2–Ce4+O2 is small in comparison with the materials mentioned above, then it can withstand the composition change of the exhaust gas.5–7) Solid solution of ceria doped with other cations would also have the enhanced capability of oxygen store and release.8–11) Especially, dissolving ZrO2 in the CeO2 is one of the most effective methods for increasing oxygen storage capacity (OSC).10–12) Furthermore, fully dissolved solid solution between ZrO2 and CeO2 has larger OSC. Trovarelli et al. showed the CeO2–ZrO2 solid solution made by hard milling in dry condition has a good OSC.13) CeO2–ZrO2 solid solution made by attrition milling in wet condition has finer particle size and larger specific surface area.14,15) Particularly the solid solution made by wet-attrition mill process would be excellent for the purpose. However, the OSC of the solid solution has not been estimated yet.

In the present work, the capability of the material as the auxiliary catalyst, which must have the high capability of the oxygen store and release, is studied.

2. Experiments

2.1 Material preparation

Material was prepared by the near room temperature process with the attrition mill:14) High purity ceria (CeO2) (purity: 99.9%) was milled in the attrition mill made of 3 mol% Y2O3-doped zirconia (ZrO2) with the balls of the same composition, in ethanol. Selecting the suitable milling time, the solid solution, Ce1-x(Zrx)O2, of any given composition (x) was prepared. The material by the conventional solid–solid reaction process at high temperature was also made for comparison: ZrO2 was added to CeO2 powder in the following way. CeO2 powder (10 μm in the average size) of high purity (99.9%) was soaked in aqueous solution of zirconium oxide nitrate, then neutralized with aqueous solution of ammonia, then mixed in a ball mill, and then the mixture was heated up to 700°C to get the solid solution between them.

The catalyst, 1 mass% of platinum black, was added on
the surface of the prepared materials, to study the interaction between the catalyst and the materials. The addition was made by dipping the solid material into the aqueous solution of Pt(NO)\(_2\)(NH\(_3\))\(_2\) and diluted nitric acid, and then it was cured for 2 h in air at the temperature of 500°C.

### 2.2 Measurement of the capability of storing and releasing oxygen

The solid solution powders with and without 1 mass% of platinum black were reduced by 20% H\(_2\) (N\(_2\) balance) followed by oxidation in 50% O\(_2\) (N\(_2\) balance) at 500°C, and the weight loss and gain was measured by therogravimeter before and after each reduction and oxidation. The time to reach the saturation was also measured, with and without platinum black.

Furthermore, the solid solution powders made by milling process, with 1 mass% of platinum black, was preheated in 50% O\(_2\) (N\(_2\) balance) at 800°C for 2 h, then cooled to the room temperature. After cooling, they were heated in 20% H\(_2\) (N\(_2\) balance) in stepwise of 100°C from 200°C to 900°C, in which the keeping time for each step was 5 min, when measured it using material with platinum black, while, in which that was 120 min, measured it using material without platinum black. The keeping time to reach the saturation had been decided after some previous trials. Then, the cumulative value of the loss was taken as the value of oxygen released for each material at the temperature.

### 2.3 Analysis of prepared material

Crystals present in the prepared material were identified by X-ray diffraction method. For that, Rigaku RINT2200 was used.

### 3. Results and discussions

#### 3.1 Materials resulted from the milling process and conventional high temperature process

Result of the analysis of the material prepared by the milling process by X-ray diffraction method revealed that it was composed of the solid solution, Ce\(_{1-x}\)(Zr\(_x\))O\(_2\). The lattice constant of the solid solution is shown in Fig. 1 (indicated by ◆). The constant makes a linear line against the amount of weight gain in the process or the supplied zirconia in agreement with Vegard’s law,\(^{10}\) which proves the material is just the solid solution and the valence of cerium as well as zirconium is 4. The constant of the conventionally prepared one does not follow Vegard’s law, when it was plotted against the amount of added zirconia. The constant for the material with content of 50 mol% ZrO\(_2\) is 0.537, which corresponds to 18 mol% of ZrO\(_2\) content. So the fact means that the rest (32 mol%) of ZrO\(_2\) remains not dissolved in cerium oxide. The presence of undissolved zirconium ions in the conventionally prepared material is due to the difficulty of the dissolution in the solid–solid reactions.

#### 3.2 Interaction of the solid solution with catalyst, Pt

The weight loss as well as the gain of the specimen with platinum black increases rapidly to 95% or so of the value of saturation and reaches the saturation in a few minutes. The time to reach the saturation of storing (t\(_s\)) and releasing (t\(_r\)) oxygen was measured under 50%O\(_2\) (N\(_2\) balance) and 20%H\(_2\) (N\(_2\) balance) atmosphere. The results are shown in Table 1, for the solid solution powder made by 29 h’s milling process (containing 50 mol% ZrO\(_2\)) with and without 1 mass% of platinum black, as a typical example. t\(_s\) for the gain of the specimen without platinum black is the same as that of the specimen with platinum black. However, t\(_r\) for the loss of that without platinum black took much longer time (90 min) to the saturation. Other specimen shows almost the same behavior.

The time, t\(_s\), for the saturation in releasing is very long for each material without platinum black, as described above, and it is largely improved, by 30 times under the presence of platinum black. This result shows that platinum black acts as the catalyst for atomization or ionization of hydrogen molecule to react with oxygen ion at the surface as well as in the lattice of the solid solution, or to force those oxygen ions to migrate and react easily with hydrogen around the platinum black particle. The time of the specimen without platinum black for the saturation, t\(_s\), is the same as the time, t\(_r\), of the specimen with platinum black. This fact shows that the activation by the catalytic reaction for rapid reaction is not necessary in storing oxygen, or for the oxidation of Ce\(_{3+}\) to Ce\(_{4+}\). The capacity of storing and releasing oxygen of each material does not depend on the presence or absence of platinum black. Platinum black affects only the reducing process of the solid solution.

#### 3.3 Capability of the storing or releasing oxygen of the solid solutions

The amount of the stored or released oxygen of the solid solution (OSC; oxygen storage capacity) prepared by milling process is shown in Fig. 2, comparing with the material made by conventional heating method, as a function of ZrO\(_2\) contents in the material. As shown in Fig. 2, the value of OSC increases with ZrO\(_2\) content in the lower ZrO\(_2\) region, and keeps constant in relatively higher ZrO\(_2\) content region. The maximum value of OSC of the material by milling

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**Table 1. Time to Reach the Saturation of Storing and Releasing Oxygen and the Amount of Oxygen Stored or Released**

<table>
<thead>
<tr>
<th>Time or amount</th>
<th>with Pt</th>
<th>without Pt</th>
</tr>
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<tbody>
<tr>
<td>Saturation time under oxidation condition in 50%O(_2)/N(_2) (\text{Js})</td>
<td>3 min</td>
<td>3 min</td>
</tr>
<tr>
<td>Saturation time under reduction condition in 20%H(_2)/N(_2) (\text{Jr})</td>
<td>3 min</td>
<td>90 min</td>
</tr>
</tbody>
</table>

**Amount of oxygen stored or released**

<table>
<thead>
<tr>
<th></th>
<th>μmolO(_2)/g-catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>384</td>
<td>μmolO(_2)/g-catalyst</td>
</tr>
</tbody>
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**Fig. 1.** Lattice constant of Ce\(_{1-x}\)Zr\(_x\)O\(_2\) solid solution as a function of ZrO\(_2\) content (◆), or the amount added (◼). Ce\(_{1-x}\)Zr\(_x\)O\(_2\) solid solution synthesized by milling CeO\(_2\) powder with ZrO\(_2\)-balls in ethanol, ◆ cubic ZrO\(_2\) (source: JCPDS27-0997)
process is 3 times larger than that by conventional heating method. This result shows that solid solution of CeO2 and ZrO2 have higher OSC than the heterogeneous material of the same composition. The value of OSC, 150 μmol O2/g, of the material, by conventional heating method, containing 16.7 mol% of ZrO2 corresponds to that of the material, made by milling process, containing 6 mol% of ZrO2. So approximately 10 mol% of ZrO2 is present in the material isolatedly from the solid solution phase. The lattice constant of the material, by conventional heating method, containing 50 mol% of ZrO2 is 0.537 nm which corresponds to that, by milling process, containing 18 mol% of ZrO2 having OSC of 250 μmol O2/g. This shows that ceria (50 mol% of the total) makes solid solution of 18 mol% ZrO2, and the rest of ZrO2 is isolated in the material. The net amount of ZrO2 in the solid solution is 11 mol% (=18/82×50) and the isolated ZrO2 is of 39 mol%. The amount of OSC for the material prepared by solid−solid reaction is about 150 μmol O2/g, as shown in Fig. 2. The expected amount of OSC for the material having 50 mol% ceria as solid solution (18 mol% ZrO2) can be estimated on the basis of the amount (50 mol% CeO2) and the amount of OSC (250 μmolO2/g) of the solid solution as 152 μmolO2/g(=250×(50/82)). The value agrees well with the observed value, 150 μmol O2/g, which proves the compatibility of the results.

3.4 Temperature dependence of OSC

Temperature dependence of OSC of the solid solution, made by milling process, with platinum black is shown in Fig. 3. The lines made by the least square method is also shown in the figure. The OSC at a given temperature has the tendency to increase monotonously with increasing ZrO2 content. OSC also increases with increasing temperature.

OSC measured by this method is thought to be the value in equilibrium, so, the OSC in Fig. 3 is directly related to the nonstoichiometry of cerium oxide. Therefore the increase of OSC with temperature means the increased occurrence of the change of nonstoichiometry in CeO2 with the temperature. In CeO2, the nonstoichiometry is related to the occurrence of oxygen vacancy. Then the increase of OSC with temperature is in good agreement with the previous study that oxygen vacancies occur more easily at higher temperature in cerium oxide.\(^\text{(5,7)}\)

The extrapolation of the data belonging to the same temperature, to the point of 100% ZrO2 shown in Fig. 3, gives the same value, 0.25 mol O2/mol Ce for the temperatures from 500°C to 900°C. The value, 0.25 molO2/molCe, can be realized only when every cerium ion varies from 4 to the valence of 3. Therefore, the cerium ion changes completely to the valence of 3 in the extremely diluted solid solution. Below 500°C the change to the valence of 3 becomes incomplete.

As shown in Fig. 3, only 30% of Ce ion in pure cerium oxide can be reduced to the valence of 3, even at the temperature of 900°C. The value of the capacity decreases gradually when the temperature is lowered to 500°C. The value in the temperature range lies between the value of the extremely diluted solid solution and that of pure cerium oxide, depending on the content of ZrO2 in the solid.

Concerning the capacity shown in Fig. 3, the value at the temperature, T, for the solid solution with x mol% ZrO2, \(Q(x,T)\), can be expressed approximately as follows:

\[
Q(x,T) \approx (100-x)q(0,T) + xq(100,T)/100
\]  
(1)

The variables, \(q(100,T)\) and \(q(0,T)\) stand for the value of the solid of pure cerium oxide at \(T\), and that of the extremely diluted solid solution, respectively.

The dependence of the capacity on the ZrO2 concentration in the solid means that the presence of Zr ion enhances the oxygen vacancies occurred in the valence of 3 in Ce ion. The effective ionic radii of each ion, Ce\(^{4+}\), Ce\(^{3+}\), Zr\(^{4+}\) and O\(^{2-}\) are 0.097 nm, 0.114 nm, 0.084 nm and 0.138 nm, in their coordination number of 8, 8, 8 and 4, respectively, based on that of O\(^{2-}\)(0.140 nm) in the coordination number of 6.\(^\text{(10)}\) So the change of 4 to 3 in the valence of cerium ion results in the volume increase, which would restrict further change due to the increased stress energy. The presence of the smaller ion of Zr\(^{4+}\) could compensate the volume increment and the restriction. This would be the main reason why the presence of Zr ion enhances the valence change (4+→3+) in Ce ion and the increase of OSC. In the release process, the release of oxygen should start in the full dense solid, and the release would not be easy. On the other hand, in the store process, oxygen should migrate into the solid, under the presence of some oxygen vacancies, which would make the migration easier than in the release process. These would be responsible for \(t_r-t_s\). Under the presence of Pt black, H\(_2\), CO, and also H\(_2\)O is rapidly oxidized which means these reductive molecules or O\(^{2-}\) are activated by Pt. The escape out of
oxygen from the solid needs the transfer of electron from oxygen to Ce$^{4+}$, making the valence of Ce$^{4+}$ to 3(Ce$^{3+}$), and to react with H and C. In the process, the reductive molecules would play some important roles to take off oxygen, and this would be made by the form of atomic or ionic form of H and C rather than molecular form. Pt would activate these processes, and make the reaction time shorter. On the other hand, in the store process, the migration of oxygen into the solid only needs the transfer of electron from Ce$^{3+}$ to oxygen in the process, which is much simpler process than that in the release process. The simpler process will be responsible, together with the presence of vacancies and smaller Zr ions, for the shorter time of $t_s$ than $t_r$.

4. Conclusion

Oxygen storage capacity (OSC) of the ceria-zirconia solid solution prepared by the near room temperature process of attrition milling and the material of the same composition, made by conventional high temperature process, was studied by adding 1 mass% or none of platinum black and the following was concluded.

1. The solid solution of ceria-zirconia has excellent OSC value of about 400 $\mu$mol O$_2$/g, which is 2.7 times larger than the heterogeneous material prepared by conventional heating method, which has the same composition and composed of solid solution of less ZrO$_2$ and isolated ZrO$_2$.

2. The increase of ZrO$_2$ content in the solid solution caused the increase of OSC below 40 mol% of zirconia content in the solid solution.

3. The amount of released O$_2$ molecule per cerium ion, in the ceria-zirconia solid solution, increased linearly with zirconia content and also increased with temperature. The extrapolation of the lines belonging to the same temperature to the point of 100% ZrO$_2$, above 500°C, gives the value of 0.25 mol O$_2$/mol Ce, which corresponds to the value of one cerium ion of the valence of 3 in infinite dilution in ZrO$_2$.

4. The increase of OSC of cerium ion with zirconium ion in the solid solution is thought to be caused through compensation of volume increase in the valence change, Ce$^{4+}$ → Ce$^{3+}$, which would restrict further change, by the presence of open volume introduced by the smaller ion (Zr$^{4+}$).

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