Flowability control of bed materials in a fluidized bed reactor for solar thermochemical process

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Abstract

Hydrogen production by solar thermochemical process uses concentrated solar radiation as its energy source. Various thermochemical processes operating at technically manageable temperatures which are a solar thermochemical two-step water splitting and solar gasification of carbonaceous material have been extensively studied and demonstrated by researchers around the world. These processes are capable of converting high-temperature heat from concentrated solar radiation into clean hydrogen from water. In this study, in order to control a flowability (fluidization state) of bed materials in a fluidized bed reactor for thermochemical processes (two-step water splitting cycle and gasification of coal coke), firstly, a basic relationship between pressure drop of inlet gas and gas flow rate was experimentally examined using bed materials with different particle sizes by a small-scale quartz reactor at ambient pressure and temperature. Secondly, the CeO\textsubscript{2} particles having the size determined by above-described flowability test were tested using a windowed fluidized bed reactor prototype. The fluidized bed of CeO\textsubscript{2} particles was exposed to a concentrated Xe light by sun-simulator with an input power of about 5 kW\textsubscript{th} for the T-R step in order to release oxygen. The production rate and productivity of oxygen and the reactivity of CeO\textsubscript{2} particles were examined in this paper.

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1. Introduction

Various solar thermochemical processes, for example, thermochemical water splitting cycle, solar gasification of carbonaceous material and solar reforming of methane et al. have been proposed and demonstrated for the purpose of converting concentrated solar high-temperature heat into clean hydrogen in sunbelt or solar belt regions [1]. Among the processes, a solar thermochemical two-step water-splitting is a simple method, operating at technically manageable temperatures by use of a metal oxide as a redox medium for the cycle, which is capable of producing hydrogen from water [2]. Also, a solar gasification of carbonaceous material contains highly endothermic chemical reactions [3]. Thus, solar gasification is a promising key technology for thermochemical conversion, which can produce clean chemical fuels by using high-temperature solar heat. The greatest advantage of solar-driven gasification is the storage of a significant fraction of solar energy as the chemical energy of the synthesized fuel molecules, and the fuels can reduce the net CO₂ emissions to the environment and conserve fossil fuels [4].

Hydrogen productivity and cyclic reactivity of thermochemical two-step water-splitting using CeO₂/CeO₂₋ₓ redox pair has been investigated by some researchers [5-10]. Several reactor concepts was proposed and demonstrated. The present authors (Niigata University, Japan) have developed “fluidized bed solar reactor” combined with solar reflective tower or beam-down optics for the solar thermochemical processes. Recently, a fluidized bed reactor prototype has been tested and demonstrated at laboratory scale for thermochemical two-step water-splitting [11-14] and coal coke gasification [15-20] using concentrated Xe light from a sun-simulator. For the thermochemical two-step water splitting [21, 22], a cerium oxide redox pair has emerged as a reactive redox material. A thermodynamic calculation for CeO₂ system [15] shows that CeO₂ can be thermally reduced at below 1500ºC to non-stoichiometric form in oxygen (CeO₂₋ₓ). In the second step of the water decomposition step, the CeO₂₋ₓ can react with steam at lower temperatures to produce hydrogen. Thus, the two-step reaction can be roughly written as follows:

\[ \text{CeO}_2 \rightarrow \text{CeO}_2 + \delta/2\text{O}_2 \quad \text{(Thermal Reduction or T-R step)} \quad (1) \]

\[ \delta\text{H}_2\text{O} + \text{CeO}_2 \rightarrow \text{CeO}_2 + \delta\text{H}_2 \quad \text{(Water Decomposition or W-D step)} \quad (2). \]

Alternatively, for the coal coke gasification, to enhance the gasification rate for a fluidized-bed reactor, quartz sand was recently investigated as a chemically inert bed material for the fluidized bed and as a thermal transfer/storage medium inside the reactor for coal coke gasification under direct light irradiation [20]. A laboratory-scale prototype windowed fluidized-bed reactor consisting of quartz sand and coal coke particles was investigated for steam gasification using concentrated Xe-light radiation as the energy source. The main reactions for the steam and CO₂ gasification of coke (carbon) are shown as follows:

\[ \text{C (coal)} + \text{H}_2\text{O(l)} = \text{CO} + \text{H}_2 \quad \Delta H_{298K} = 175 \text{ kJ/mol} \quad (3) \]

\[ \text{C (coal)} + \text{CO}_2 = 2\text{CO} \quad \Delta H_{298K} = 172 \text{ kJ/mol} \quad (4) \]

The calorific value of coal or carbon feed can be theoretically upgraded by ~45% when the process heat required to drive the reactions, as shown in Equations (3) and (4), is provided by concentrated solar radiation. Syngas obtained using solar energy can be thermochemically transformed to hydrogen by the water–gas shift reaction, to liquid hydrocarbon fuels such as diesel, kerosene, and gasoline via Fischer–Tropsch synthesis, or directly used as a combustion fuel for power generation.

In this study, in order to control a flowability (fluidization state) of bed materials in a fluidized bed reactor for thermochemical processes (two-step water splitting cycle and gasification of coal coke), firstly, a basic relationship between pressure drop of inlet gas and gas flow rate was experimentally examined using bed materials with different particle sizes by a small-scale quartz reactor at ambient temperature. Secondly, the CeO₂ particles having the size determined by above-described flowability test were tested using a windowed fluidized bed reactor prototype. The fluidized bed of CeO₂ particles was exposed to a concentrated Xe light by sun-simulator with an input power of about 5 kWth for the T-R step in order to release oxygen. The production rate and productivity of oxygen and the
reactivity of CeO$_2$ particles were examined in this paper. Presently, a scale-uped 30 kW$_{th}$ and 100 kW$_{th}$ solar fluidized bed reactors are designed and manufactured for testing 30kW$_{th}$ solar reactor by sun-simulator and 100kW$_{th}$ solar reactor by solar beam-down type concentrating system built in Miyazaki, Japan.

2. Experimental

2.1. Flowability test of CeO$_2$ particles by a small-scale quartz reactor of fluidized bed

A basic relationship between pressure drop of inlet gas and gas flow rate was experimentally examined using bed materials with different particle sizes by a small-scale quartz reactor at ambient temperature in order to examine a flowability (fluidization state) of bed materials in a fluidized bed reactor for thermochemical processes. Fig. 1 shows an experimental setup for flowability test of fluidizing particles by using a small-scale quartz reactor. The diameter of the quartz reactor tube was 25 mm with a thickness of 2 mm, and a length of 48 mm. A porous quartz frit of the porous distributor (the hole diameter is 40 $\mu$m) was positioned 18 mm above.

CeO$_2$ particles (purity: 99.9%) were purchased from Kojundo chemical Co. in Japan. Each size of CeO$_2$ particle is 30-75, 75-100, 100-300, 300-500 and 500-700 $\mu$m. These three particle sizes were used as fluidizing particles for the fluidized bed. The CeO$_2$ particle was put into the quartz reactor. The bed height of CeO$_2$ particles inside the reactor is 25 mm for all the particle size. N$_2$ was flowed upwards from the bottom of the reactor through the distributor to create the fluidization of CeO$_2$ particles under various air flow rates. A pressure difference for the inlet and outlet gas was measured under various gas flow rates by manometer. The relationship between pressure drop of fluidization gas and flow rate was experimentally examined using each size of CeO$_2$ particle.

![Figure 1. Flowability test of CeO$_2$ particles ranged in variety size by a small-scale quartz reactor.](image)

2.2. Thermal reduction of CeO$_2$ particles by a fluidized bed reactor

A thermal reduction step of two-step water-splitting using the CeO$_2$ particles ranged in size between 50 and 100$\mu$m were examined using an internally circulating fluidized bed reactor by a concentrated Xe light irradiation. Fig. 2 shows experimental set-up for thermochemical two-step water-splitting by a fluidized bed reactor. The inside diameter of the outer Inconel tube was 85.1 mm with a thickness of 2 mm. The internal centrally located draft tube of the reactor was made of Inconel, with an inner diameter of 27 mm, 2 mm thickness, and a length of 47 mm. The bottom of the draft tube was positioned 17 mm above the porous stainless steel frit of the porous distributor (the hole diameter is 40 $\mu$m).

A N$_2$ carrier gas (purity: 99.999%) was allowed to flow upwards through the tubes to create the internal circulating fluidized bed of CeO$_2$ particles and to thermally reduce CeO$_2$ particles through internal circulation to expose to irradiation. The reactor loaded CeO$_2$ particles was preheated by an electric furnace (preheater) at 900°C.
under N₂ gas stream. The preheater was controlled using a K-type thermocouple in contact with the exterior wall of reactor. After temperature of the reactor reached 900ºC under N₂ gas stream, the preheater was turned the power off before starting concentrated Xe light irradiation for T-R step. As the N₂ gas stream was passed through the distributor inside the reactor, the fluidized bed of CeO₂ particles was directly heated during 30-60 min by concentrated Xe light irradiation for T–R step. A production rate of oxygen evolved during the T-R step was measured and recorded against time course by mass spectrometry. The oxygen production profile was integrated with the reaction time, the evolved amount of oxygen was calculated. After the T-R step, a portion of the reacting particles was sampled from the several parts of fluidized bed. The sampled powders were pulverized and subjected to powder XRD with CuKα radiation for identification of the formed phases.

A high-power sun-simulator equipped with three 7 kW Xe lamps was designed and fabricated by Japanese company (Nippon Koki Kogyo co., LTD., UXL-70SC). This reactor was placed below three 7 kW Xe lamps to simulate a sun with the central axis of the reactor aligned with the axis of the oval concentrator of the sun-simulator. The concentrator of the sun-simulator reflected the Xe-lamp beam downwards to the focal spot. The top of the static bed was set on the focal spot and the focal diameter of the spot was approximately 9 cm. The intensity and distribution of the concentrated Xe beam on the spot could be varied by changing the power supply to the Xe-arc lamp. The energy flux density of the Xe beam was previously measured using a heat flux transducer with a sapphire window attachment (Medtherm, 64-1000-20).

3. Results and discussion

3.1. Flowability test of CeO₂ particles by a small-scale quartz reactor

Fig. 3 shows results for flowability tests of a fluidized bed reactor. The CeO₂ particles with different particle sizes between 30 and 700 μm diameter was used and tested as a bed material for the fluidized bed reactor. For the particle size of 30-75μm, a pressure drop initially increased with superficial gas flow velocity of inlet gas, and reached the peak of 540 Pa at a velocity of 0.041 m·sec⁻¹. Subsequently, the pressure drop was fluctuated and then decreased to about 400 Pa. This behavior of pressure drop for the superficial gas flow velocity indicates that the velocity of 0.041 m·sec⁻¹ corresponds to start a fluidization of particle bed; a minimum superficial gas flow velocity (Uₘf) = 0.041 m·sec⁻¹ for the particle size 30-75μm. Similarly, for the particle size of 75-100 μm, a peak value for pressure drop was elevated to about 700 Pa in comparison to that for the particle size 30-75μm, while the value of Uₘf slightly increased to 0.048 m·sec⁻¹. As a particle size of the bed material increased, the values for Uₘf and pressure drop at Uₘf were also elevated. According to the results in this figure, the fluidization state can be categorized into three regions: fixed layer, bubble fluidization and turbulent fluidization regions. Firstly, a pressure drop increases with increasing a superficial
gas flow velocity. This region was called to fix bed layer, and \( U_{mf} \) was corresponded to the following value for the peak of the pressure drop. It was observed that hereafter, a particle started fluidizing. By further increasing a superficial gas flow velocity, the pressure drop plateaued. In this region, a particle bed made a bubbling fluidization. Beyond the bubbling fluidization, the pressure drop increased again, a particle bed formed a turbulent fluidization. The fluidization state aimed in this study is a lower superficial gas flow velocity and a mild fluidization of a particle bed in the reactor. Thus, a bubble fluidization was targeted in this study. Based on the experiments of flowability test of CeO\(_2\) particles, the particles with a smaller size which enables it to make a bubbling fluidization under a lower passing N\(_2\) gas are favorable for the fluidized bed reactor operating a thermochemical two-step water splitting.

![Figure 3. Pressure drop of fluidized bed using various CeO\(_2\) particle size](image)

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Minimum Fluidization Superficial Gas Velocity, ( U_{mf} ) (m/sec)</th>
<th>Volumetric Fluidization Superficial Gas Velocity, ( U_{mf} ) (dm(^3)/min)</th>
<th>Pressure Drop at ( U_{mf} ) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-75 ( \mu )m</td>
<td>0.041</td>
<td>1.2</td>
<td>540</td>
</tr>
<tr>
<td>75-100 ( \mu )m</td>
<td>0.048</td>
<td>1.4</td>
<td>694</td>
</tr>
<tr>
<td>100-300 ( \mu )m</td>
<td>0.129</td>
<td>3.8</td>
<td>777</td>
</tr>
<tr>
<td>300-500 ( \mu )m</td>
<td>0.272</td>
<td>8.0</td>
<td>784</td>
</tr>
<tr>
<td>500-700 ( \mu )m</td>
<td>0.373</td>
<td>11</td>
<td>645</td>
</tr>
</tbody>
</table>

3.2. Thermal reduction of CeO\(_2\) particles by a fluidized bed reactor

Fig.4 shows the energy flux density of the incident Xe beam on the irradiated surface of the fluidized bed. For the T-R step, the central peak of the flux density reached 4225 kWm\(^{-2}\), and the average flux density on the exposed surface of the fluidized bed was 903 kWm\(^{-2}\). The input power of the incident Xe beam was 5.1 kW\text{th} for T-R step.

In this experimental campaign, Irradiation time of Xe beam and superficial N\(_2\) gas velocity were varied as a parameter to perform thermal reduction of CeO\(_2\) particles. The experimental conditions and results for the T–R step performed using a windowed fluidized bed reactor are listed in Table 2. Based on the results for the pressure drop of
the fluidized bed in order to observe and evaluate the fluidization state with various particle sizes in the Chapter 3.1, the CeO\(_2\) powder with a particle size of 50-100 \(\mu\)m was selected and used in order to enable a bubbling fluidization in the reactor in the series of testing in Table 2.

Figure 5 shows the results for experimental No. 3 in Table 2. Time variations for temperature of outer reactor wall and production rate of oxygen during T-R step at \(F = 10.0 \, \text{N dm}^3\cdot\min^{-1}\), and photograph of material sampled from the fluidized bed after the T-R step are shown. The materials were sampled from the bottom, the middle and the surface of fluidized bed. The original material before the testing and the powder sample piled up on the conical shaped-parts (aperture) of the reactor during the T-R step are also shown in this figure as reference. The evolved amounts of oxygen were 1.39 Ncm\(^3\)g\(^{-1}\) material, and the total amounts of oxygen were 1528 Ncm\(^3\). As seen in Fig. 5(b), a color of the particles was changed from white in original powder into gray color after the thermal reduction. In addition, the particle color became darker as a particle bed deepened toward the bottom of the reactor. In the experimental conditions, a small coagulating/sintering of the particles was observed after the thermal reaction inside the reactor. This result means that a fluidization of CeO\(_2\) particles is insufficient to make a stable fluidization and continuous oxygen production under the Xe-light radiation. Therefore, in order to avoid making coagulation/sintering during the T-R step, we focused on the thermal reduction of CeO\(_2\) particles at higher superficial N\(_2\) gas velocity in No. 5 listed in table 2.

Figure 6 shows the results for experimental No. 5 at \(F = 13.0 \, \text{N dm}^3\cdot\min^{-1}\) in Table 2. The evolved amounts of oxygen were 0.55 Ncm\(^3\)g\(^{-1}\) material, and the total amounts of oxygen were 526 Ncm\(^3\). As shown in Fig. 6(b), the peak due to CeO\(_2\) initially appeared only in the XRD pattern before Xe-light radiation. After the T-R step, the relative intensity of the CeO\(_2\) peak decreased, and shifted into lower diffraction angle in comparison to the original CeO\(_2\) material. The results for the peak shift indicate that a reduced phase of CeO\(_{2.5}\) was formed with a lower degree of reduction by T-R step. The extent of peak shift for the depth of the fluidized bed relatively lined up in order; top \(\approx\) middle \(\approx\) bottom depths of the fluidized bed \(>\) original material \(\approx\) powder sample piled up. The results mean that a degree of thermal reduction for the CeO\(_2\) particle is almost the same without depending on the bed depth, leading to better particle circulation inside the reactor during the T-R step in comparison to the results for No.3. Vary small and broad peak is also observed slightly at about \(\theta = 28\) degree in the XRD pattern of material obtained after the T-R step. This new peak with further greater degree of reduction in comparison to CeO\(_{2.5}\) with a lower degree of reduction may be ascribed to oxygen production for the second region of Fig. 6(b).

Figure 6(b) also shows a photograph of the fluidized bed material taken out from the reactor after the T-R step. A white color of the powder is an original CeO\(_2\) as a reference. A color of powder at the top, middle and bottom depth of the fluidized bed was gray. The color of powder was almost homogeneous except for the slightly-reduced CeO\(_{2.5}\) powder piled upon the conical shaped part of reactor (Aperture), and independent of the depth of the fluidized bed. These results mean that a fluidization of CeO\(_2\) particles occurs without a remarkable sintering and coagulating of the particles at high-temperature inside the reactor during the T-R step.
Table 2 Experimental conditions and results for the T–R step by a windowed fluidized bed reactor.

<table>
<thead>
<tr>
<th>No.</th>
<th>Flow rate of N₂ / Ndm³min⁻¹</th>
<th>Radiation time / min</th>
<th>Production rate of O₂ at a maximum / Ncm³min⁻¹</th>
<th>Production rate of O₂ at an average / Ncm³min⁻¹</th>
<th>Amount of O₂ production / Ncm⁻³g⁻¹material</th>
<th>Amount of O₂ production / Ncm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>30</td>
<td>92.1</td>
<td>-</td>
<td>0.29</td>
<td>276</td>
</tr>
<tr>
<td>2</td>
<td>8.5</td>
<td>30</td>
<td>65.3</td>
<td>23.0</td>
<td>0.60</td>
<td>688</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>60</td>
<td>62.8</td>
<td>26.1</td>
<td>1.39</td>
<td>1528</td>
</tr>
<tr>
<td>4</td>
<td>11.5</td>
<td>60</td>
<td>48.4</td>
<td>33.4</td>
<td>0.91</td>
<td>1038</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>30</td>
<td>76.3</td>
<td>12.2</td>
<td>0.55</td>
<td>526</td>
</tr>
</tbody>
</table>

Figure 5. (a) Time variations for temperature of outer wall of reactor and oxygen production rate during T-R step. The flow rates of N₂ gas were set at 10 Ndm³min⁻¹ and (b) photograph of material sampled from the fluidized bed with different depth after T-R step.

Figure 6. (a) Time variations for temperature of outer wall of reactor and oxygen production rate during T-R step. The flow rates of N₂ gas were set at 13 Ndm³min⁻¹ and (b) XRD patterns and photograph of material sampled from the fluidized bed with different depth after T-R step.
As seen in Figs. 5(a) and 6(a), it seems that the behavior of oxygen production can be divided into two regions: 1) the production rate of oxygen was greatly increased just after starting irradiation, and then fluctuated with time course of reaction. Subsequently, the production rate was gradually decreased (the periods of radiation time 0-45 min in Fig. 5(a) and 1-8 min in Fig. 6(a)); 2) the production rate was enhanced again, and subsequently decreased during the T-R step (the periods of radiation time 45-60 min in Fig. 5(a) and 8-30 min in Fig. 6(a)). These behaviors of oxygen production may be related with characteristics for a formation of reduced phase of CeO$_2$ during the T-R step. Namely, the oxygen production behavior for the first region means that oxygen would be predominately produced from surface area of the particle during the fluidization by Xe light radiation. Thus, rapid oxygen production would occur without coagulation of the particles. This will lead to a formation of CeO$_{2.8}$ with a lower degree of reduction and a peak shift of CeO$_2$ to lower diffraction angle in the XRD pattern. That for the second region means that oxygen would be dominantly released from deeper area of the particle inside during a long period of radiation time. Thus, relatively stable oxygen production rate would be realized in comparison to the initial oxygen production. This will be related to a formation of CeO$_{2.4}$ with a greater degree of reduction and of new peak as a reduced phase at lowest diffraction angle in the XRD pattern.

The period of time for the first region will depend on a superficial gas velocity and bed temperature. Based on an assumption that bed temperature was constant independent of radiation time and homogeneous at all depth of the bed, as a superficial gas velocity was elevated, a smooth particle circulation will be realized in then reactor. Then, the surface of the particle will be further subjected to radiation and oxygen will be rapidly released. Therefore, it is considered that the period of time for the first region was shorter for the experimental No. 5 than for the experimental No. 3.

4. Future plan

In principle, the fluidized bed reactor using the CeO$_2$ particles can perform a successive two-step water-splitting of T-R and W-D steps in a single reactor by switching the feed gas from an inert gas in the T-R step to steam in the subsequent W-D step. In the next step of this testing, a successive two-step water-splitting will be tried using the same reactor by switching the feed gas and changing the input power of incident Xe beam. The following experimental conditions will be used for the T-R step in the next step. Namely, the N$_2$ gas flow rates during T–R step were set at $F_{\text{ann}}=10.0$ N dm$^3$·min$^{-1}$; concentrated Xe light irradiation for T-R step; the CeO$_2$ particle size was 50-100 μm. Following T-R step irradiation, the input power of the incident beam was turned off briefly. Subsequently, the gas passing through the reactor is switched from N$_2$ gas to an H$_2$O/N$_2$ gas mixture; this was then introduced into the reactor for W–D step. The H$_2$O/N$_2$ gas mixture was produced by a steam generator to put in the reactor. The H$_2$O/N$_2$ gas mixture from the steam generator can be produced by passing N$_2$ gas flow through distilled water at about 100 ºC. Concentrated Xe light irradiation for W-D step was then resumed using the same sun-simulator but at a lower input power.

A newly developed solar reflective tower or beam-down optics [23, 24] was proposed as a promising solar concentrating system for solar fuel production [25, 26]. The fluidized bed reactor will be scaled up in 30 kW$_{th}$ and 100 kW$_{th}$ stages for solar testing of thermochemical two-step water-splitting and gasification of coal cokes by a beam-down type sun-simulator constructed in Niigata University and solar concentrating system built in Miyazaki, Japan.

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