| Research Paper | 研究論文 |

Two-step carbon dioxide thermochemical splitting using foam device of ceria and hercynite

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Abstract

This study describes the experiment of thermochemical splitting of carbon dioxide using the redox reaction of nonstoichiometric compound, ceria and hercynite (generally iron aluminate, $Fe_{33}Al_{67}$, in Fe-Al-O space). The reactive foam devices of ceria and hercynite were sintered through the replica method. The devices were kept in the receiver reactor, and they were irradiated by the concentrated light from the sun simulator. The temperature at the reduction process was changed up to beyond 1600℃. In the non-isothermal experiment, the temperature control with holding near the peak level increased the reaction in the case using ceria as reactive material. In the isothermal experiment, the reaction of hercynite is relatively slow compared with that of ceria. However, the change in nonstoichiometry of hercynite surpassed that of ceria. It was indicated that hercynite released twice as much gas as ceria of the same mass.

Keywords: Hercynite, Foam device, Concentrated solar simulator, Thermochemical splitting, Redox

1. Introduction

The redox reaction of nonstoichiometric compound is applicable for thermochemical splitting of carbon dioxide to synthesize liquefied fuel [1-4]. The reaction can occur without electricity and only with thermal energy, which is suitably provided by the concentrated sun light [5]. Recently, CCS (carbon capture and storage) started to collect carbon dioxide and store in the deep underground for reducing the global warming gas in the atmosphere. The thermochemical process is promised for recycling carbon dioxide captured by CCS into fuel to realize CCU (carbon capture and utilization).

Highly concentrated sun light can create high temperatures above 1000 degree Celsius using a volumetric receiver [5]. Typically, the volumetric receiver is made of a honeycomb monolith of nonreactive material like SiC. Researchers fabricated a volumetric receiver reactor of nonstoichiometric compound which directly absorbs concentrated sun for the endothermic process in the reduction step.

Marxer et al. used an octagonal cavity reactor for the thermochemical splitting of carbon dioxide[2]. They manufactured foam device of ceria, and demonstrated at the temperatures ranging between 900 and 1500 degree Celsius. Haeussler et al. experimented a solar reactor consisting of four cylindrical layers of porous ceria with different cell densities [3,4]. The annular and circular ceramics, stacked and fixed, increased the amount of the reactive material. This configuration could maintain its shape even after long time of experiment. Ceria was also useful for the thermochemical splitting water to produce hydrogen. The present study focuses on its performance for carbon dioxide splitting because of the growing interest for carbon dioxide capture and utilization.

This study experimented the thermochemical carbon dioxide splitting using ceria and hercynite [6, 7] as a redox material. The previous studies [6, 7] experimented on powdered hercynite to reveal high reactivity at the equilibrium state. The present study sintered the foam device of hercynite and ceria using replica method [8, 9]. The experiment was conducted for the foam device in the nonequilibrium when irradiated by the concentrated light. The reduction temperatures were changed in the broader range including very high levels beyond 1600℃. Such high temperatures were selected since the previous studies set relatively low temperatures at 1500℃ or below. The exhaust gas was analyzed to reveal the concentrations of product gases. The reactivity of the foam device is evaluated through the

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changes of nonstoichiometry.

2. Experimental methods

2.1 Experimental setup

Figure 1 shows general view of the experimental setup. The solar simulator irradiates a reactive foam device in a receiver reactor. The irradiation creates the sensible heat for the two-step reaction. The reaction may be written in the case of oxygen-deficient nonstoichiometric compound as

$$MO_{2-\delta_{ox}} \rightarrow MO_{2-\delta_{red}} + \frac{\Delta\delta}{2}O_2 \quad (1)$$

$$MO_{2-\delta_{red}} + \Delta\delta CO_2 \rightarrow MO_{2-\delta_{ox}} + \Delta\delta CO \quad (2)$$

Reduction reaction (1) is endothermic, and oxidation reaction (2) is exothermic slightly. The apparatus conducted the reduction and the oxidation alternately. Argon was provided to the reactor as a purge gas in the reduction step. Carbon dioxide was provided as reactant in the oxidation step. The flow rate of each gas was controlled by a mass flow controller. The gases were then passed through a receiver reactor. The exhaust gas was analyzed by a magnetic oxygen analyzer, and an infrared carbon monoxide analyzer. The micro gas chromatograph was used for validate the gas analyzers.
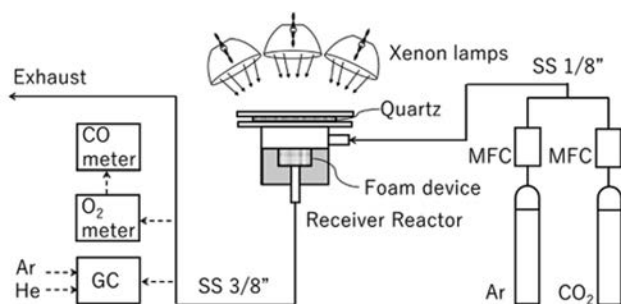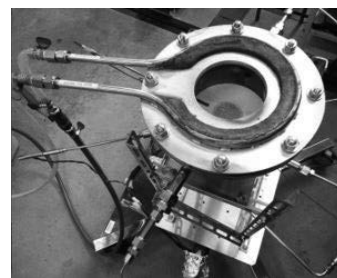

Fig. 1 Schematic diagram of the entire experimental apparatus

Figure 2(a) shows the solar simulator. The simulator irradiates 5 kWth power to a circle of 70 mm in diameter. Its average heat flux is about 1300 kWth/m². The receiver reactor is shown in Fig. 2(b). The experimental apparatus is mounted on an XY-stage. The major parts of the apparatus are SUS310S. The inside is stuffed with insulating material, supporting a circular foam device in the center. Gas flows in the apparatus from the two inlet tubes, passes through the porous device, and exits from the outlet tube. A quartz glass is fixed between gaskets and flanges, through which concentrated light enters the reactor to impinge onto the reactive device. During experiment, coolant water cools the top flange and the quartz glass. A R-type thermocouple measures the temperature just below the foam device.

(a) Solar simulator   (b) Receiver reactor

Fig. 2 Photograph of experimental apparatus

2.2 Reactive material

The powders of ceria and hercynite are used to create foam devices. The ceria powder is CE003PB (Kojundo Chemical Laboratory CO., LTD.), 99.9% purity, 7.5 μ m median diameter. The hercynite is the product of the same company, 1.6 μ m median diameter. The hercynite powder was characterized by X-ray diffraction (XRD, BRUKER table-top X-ray diffractometer D2 PHASER) at $2\theta = 20°\sim80°$, which is installed at Niigata University. XRD results for the hercynite powder are shown in Fig. 3. In the figure, the peaks of XRD corresponds well to the experiment by Millican [6] and the purity of the material was thus vindicated.
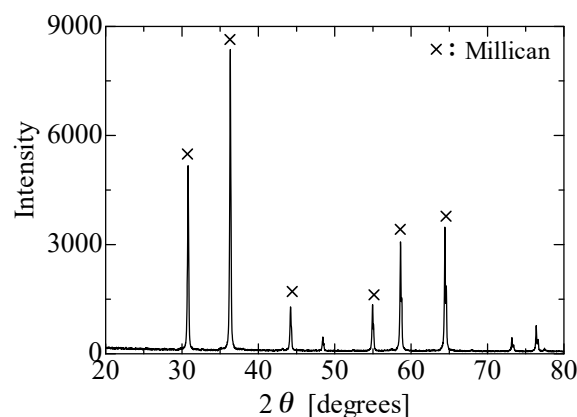

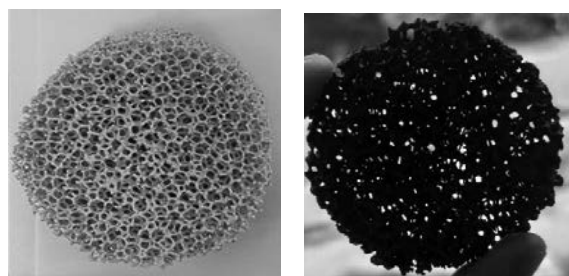Fig.3 XRD analysis of hercynite with indication of peak positions by Millican [6].

2.3 Replica method

Foam devices of ceria and hercynite are sintered by the replica method [8]. The powder of each reactive material is mixed with water and dispersant using a ball mill. The resulting slurry was stilled and heated using a magnetic stirrer while the temperature raised to 100 °C. The slurry was added polyvinyl alcohol during stirring, and this was cooled in room temperature. The slurry was impregnated into a PU (polyurethane) sponge cut circularly. The sample was dried in the room temperature for more than 24 hours.

The sample was baked to remove PU, and the remained

ceramics were sintered to foam device. The pre-firing was performed in a muffle furnace (YAMATO/FO50). In this furnace, the temperature was increased at 600°C/h and the sample was heated at 600°C for 2 hours to burn off the PU sponge. The temperature was further increased to 1150°C at 275°C/h, and the samples were fired at 1150°C for 2 hours, after which the equipment was cooled naturally to room temperature. After the pre-firing, a box furnace (Koyo Thermo System/KBF624N1-18) was used for sintering the sample. In this process, the temperature was raised to 1150 °C at 120 °C/h, then raised to 1600 °C at 60 °C/h, and kept at 1600 °C for 2 hours. Finally, the equipment was cooled naturally to room temperature.

To increase the porosity of the porous material, 5.0% carbon was added to the ceria slurry. In this study, experiments were conducted with cell densities of 8ppi (pores per inch) with or without carbon. Photographs of porous ceria and hercynite are shown in Fig. 4 (a, b), respectively.

(a) Ceria   (b) Hercynite
Fig. 4 Photographs of porous device

2.4 Experimental procedure

The receiver reactor is purged by a stream of argon at the beginning of the experiment. The solar simulator starts to irradiate the reactive device when the material is reduced to release oxygen in argon atmosphere. Then, the stream of argon is switched by carbon dioxide, and the substance is oxidized to release carbon monoxide.

Temperature was controlled in three ways. Non-isothermal experiment controls temperature below the device changing the power of solar simulator. The level of power is kept at 90 % during the reduction. When the temperature reaches the upper criterion (1500～1600℃), the reduction step changes to the oxidation step. Then, the level of simulator is decreased to 50 % to let the temperature decrease to the lower criterion (1000～1200 ℃). Non-isothermal experiment holding temperature proceeds similarly. The procedure controls the power of the simulator to keep the criteria of temperatures so that the concentration of product gases decreases below 0.1 %. Isothermal experiment regulates the level of simulator to keep the same temperature according to the prescribed condition.

The experimental conditions are shown in Table 1. Experiments numbered 1 through 6 are non-isothermal cycling experiments, of which the peak temperature during the reduction reaction was maintained in experiments 1 through 3. Experiment 7 was performed under low-temperature reduction conditions and isothermal cycling to compare with the hercynite device experiments. Experiments 7 through 9 were performed for one cycle only. The flow rates of Ar and CO_2 are 7.0 L/min through the experiment excluding third and fourth cycles of N3. In two

Table 1 Experimental conditions

No.	Temperature condition	Peak temperature control	Reactants	Mass [g]	Carbon [%]	Porosity [%]	T_{red} [°C]	T_{ox} [°C]
1	non-isothermal	not holding	Ceria	46.6	-	83.5	1429~1505	945~1038
2				55.3	-	85.2	1601~1602	999~1000
3				55.3	-	85.2	1559~1595	1212~1287
4		holding		52.7	-	81.4	1517~1641	1252~1369
5				57.3	5.0	86.5	1552~1566	998~1000
6				57.3	5.0	86.5	1599~1605	999~1023
7	isothermal			101.4	-	74.7	1361	1359
8			Hercynite	18.48	-	82.3	1311	1305
9				18.48	-	82.3	1364	1355

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cycles the flow rates of gases were regulated at 10.0 L/min. The pressure in the reactor was slightly positive due to the pressure loss in the exhaust tube through all the cases.

3. Results and discussion

3.1 Gas generation rate from ceria

Figure 5 shows the experimental result in the case of non-isothermal experiment where the temperature is controlled without holding. The figure shows temperature and the generation rate of oxygen and carbon monoxide. In the figure, temperature increases and decreases according to the control of solar simulator with spikes of 1559 – 1595 ℃ and minima of 1212 – 1287 ℃ in four cycles. There are generation of oxygen at the higher temperatures indicating the reduction of ceria. Generation of carbon monoxide at the lower temperatures results from the oxidation of the material. The experiment demonstrates that carbon dioxide is separated into oxygen and carbon monoxide by the cycle of redox reaction.

Another experiment is shown in Fig. 6 for the case of holding temperature. The cycle time increases due to the temperature control. The generation of oxygen and carbon monoxide are more remarkable than the case of not holding temperature.
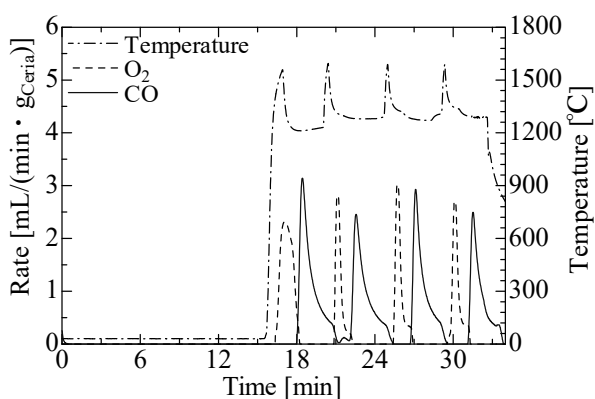

Fig. 5 Temperature and gas generation rate from ceria in the case of not holding temperature (N3)
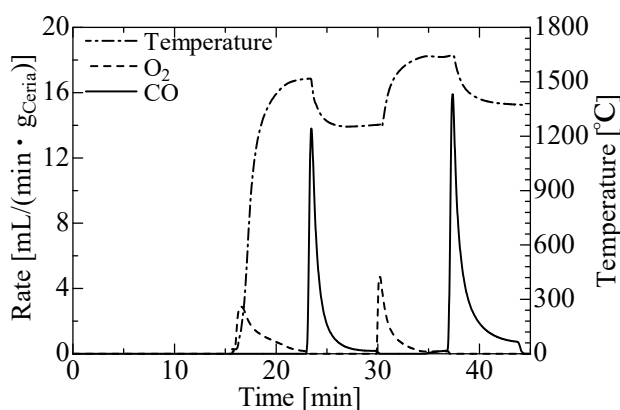

Fig. 6 Temperature and gas generation rate from ceria in the case of holding temperature (N4)

Figure 7 shows the result from the case of holding temperature with the foam device sintered with carbon. The generation rate of gases is still in the higher level than the case of not holding temperature. However, there is not clear effects from the carbon addition to the foam device. The experiment demonstrated that the temperature control is essential for the reaction rate in the thermochemical splitting of carbon dioxide.
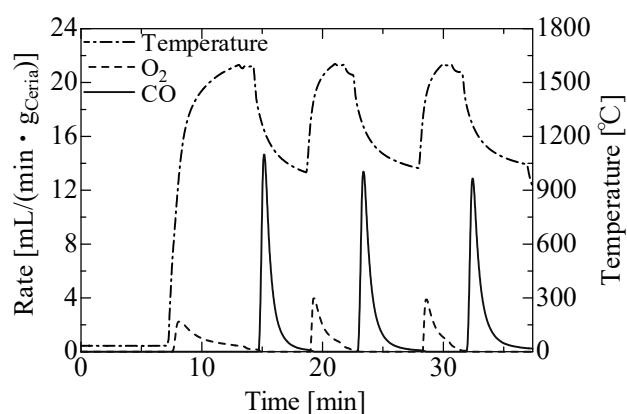

Fig. 7 Temperature and gas generation rate from ceria in the case of holding temperature (N6)

3.2 Comparison between hercynite and ceria

The preliminary experiment suggested that the foam device of hercynite was suitably tested at the lower level of temperatures since the material is more likely to be broken than ceria due to the low melting point. It was also suggested that hercynite fits the iso-thermal cycle since the non-isothermal cycle in the case of lowered temperatures resulted in very slow reaction in the oxidation. Therefore, the isothermal experiment was conducted for the hercynite device.

Figure 8 shows the experiment of hercynite device. The temperature is kept at 1300℃ isothermally. The gas generation rate is not so high as that of ceria in the case of higher temperatures. However, the gas generation continues for longer periods in both of reduction and oxidation steps. The time intervals in each reaction are about 30 minutes. The reaction may continue for longer time. However, two steps of reaction were ended so that the total time be within 75 minutes for safety of operation. This is because the longer experiment resulted in frost on the regulator of CO_2 gas.

The experiment of hercynite at 1350℃ is shown in Fig. 9. The generation rate of oxygen becomes more conspicuous than the case at 1300℃. The generation rate of oxygen becomes larger as the temperature increases. That of carbon monoxide decays mildly and increases again during the oxidation process. In this experiment, the time interval of reduction is 20 minutes, and that of the oxidation is 55 minutes. The interval of reduction was decreased since the oxygen generation decays clearly. This

and previous experiment proved that the hercynite device is capable to split carbon monoxide through thermochemical cycle.
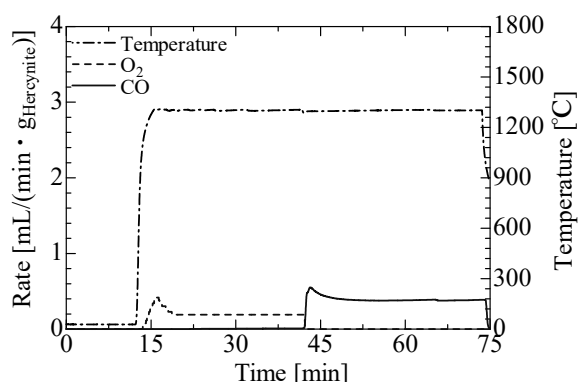

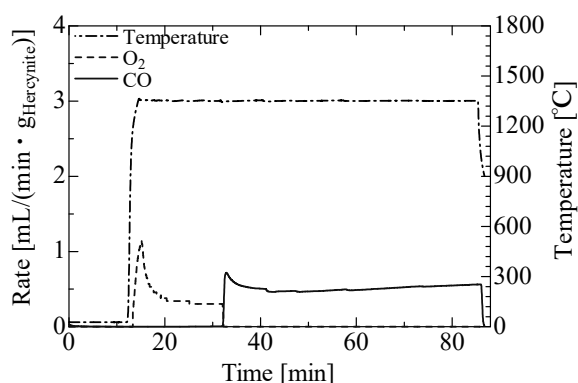Fig. 8 Temperature and gas generation rate from hercynite in the case of holding temperature (N8)

Fig. 9 Temperature and gas generation rate from hercynite in the case of holding temperature (N9)
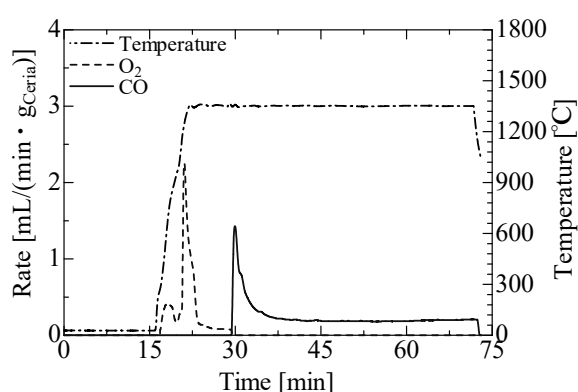

Fig. 10 Temperature and gas generation rate from ceria in the case of holding temperature (N7)

The foam device of ceria was tested in a similar manner to hercynite for comparison between different substances. Figure 10 shows such experimental result of ceria at isothermal temperature of 1350 ℃. The experiment at such a low temperature is meaningful since the receiver efficiency is expected to increase because of the attenuation of the reradiation
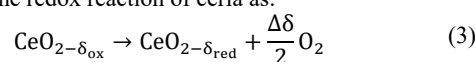
loss. The ceria device shows the higher peaks of gas generation rate of oxygen and carbon monoxide than the hercynite device. The gas generation rate rapidly increases and decreases near the peaks. It is thus suggested that the reaction of ceria occurs faster than that of hercynite. However, comparing the result in the period of low generation rate, the hercynite device is found to maintain the higher level of the generation rate than ceria in longer time. Therefore, the hercynite device is indicated to have the more capability of the reaction with the relatively slow reaction rate.

3.3 Nonstoichiometry

The reactivity of the materials is evaluated using the volume of carbon monoxide produced at the oxidation step. The volume of carbon monoxide per the mass of the reactive material and the reaction time is shown against the peak temperatures during the reduction in Fig. 11.
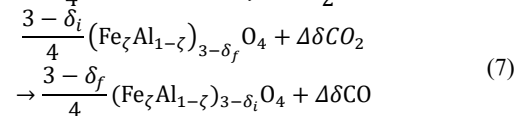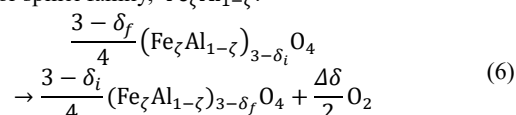
In Fig. 11, the reaction rate of ceria is separated between the case of holding temperature and the case of not holding temperature. The quantities are at 2 mL/(min g) or above in the former, whereas they are below 2 mL/(min g) in the latter. The discrepancy becomes clearer and larger as the temperature increases. It is thus suggested that the temperature control becomes more important as the temperature increases. The reaction rate of hercynite is in the same level of ceria at 1300℃ and this increased beyond ceria at 1360℃.

The previous studies treated the reaction of ceria so that the lattice of the material made vacant holes of oxygen when releasing oxygen gas [3, 4]. This paper follows this concept to describe the redox reaction of ceria as:

$$CeO_{2-\delta_{ox}} \rightarrow CeO_{2-\delta_{red}} + \frac{\Delta\delta}{2}O_2 \qquad (3)$$

$$CeO_{2-\delta_{red}} + \Delta\delta CO_2 \rightarrow CeO_{2-\delta_{ox}} + \Delta\delta CO \qquad (4)$$

$$\Delta\delta = \delta_{red} - \delta_{ox} \qquad (5)$$

In the equations, $\Delta\delta$ represents the change in non-stoichiometry. The nonstoichiometry δ increases when the material is reduced. Whereas, hercynite is modeled as a cation-deficient compound in reference to the literature [6, 7]. The redox reaction may be written for spinel family, $Fe_\zeta Al_{1-\zeta}$:

$$\frac{3-\delta_f}{4}\left(Fe_\zeta Al_{1-\zeta}\right)_{3-\delta_i}O_4$$
$$\rightarrow \frac{3-\delta_i}{4}(Fe_\zeta Al_{1-\zeta})_{3-\delta_f}O_4 + \frac{\Delta\delta}{2}O_2 \qquad (6)$$

$$\frac{3-\delta_i}{4}\left(Fe_\zeta Al_{1-\zeta}\right)_{3-\delta_f}O_4 + \Delta\delta CO_2$$
$$\rightarrow \frac{3-\delta_f}{4}(Fe_\zeta Al_{1-\zeta})_{3-\delta_i}O_4 + \Delta\delta CO \qquad (7)$$

$$\Delta\delta = \delta_i - \delta_f \qquad (8)$$

For hercynite, $\zeta = 0.333$. The nonstoichiometry δ increases at the oxidation. The changes of $\Delta\delta$ were calculated from each formula assuming $\delta_{ox} = 0$ for ceria and $\delta_f = 0$ for hercynite.

The changes in nonstoichiometry are evaluated using the

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volume of carbon monoxide. The values are shown against the maximum temperatures during the reduction step in Fig. 12. The figure includes the theory of ceria in the case of equilibrium for three levels of oxygen partial pressure. The theoretical values are calculated using the steady state model of Muhich et al. [10]. In the figure, the experimental result corresponds to the theory for the oxygen partial pressure ranging from 10^{-8} to 10^{-4} atm. Also, hercynite indicates the higher levels of nonstoichiometry than ceria. Hercynite thus shows the excellent performance in the low temperature ranges in terms of nonstoichiometry.
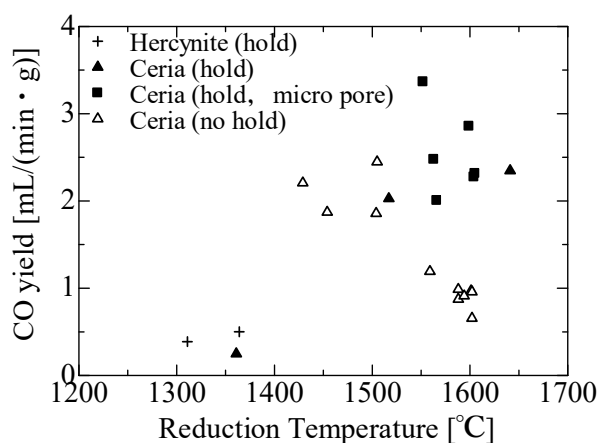
replica method. Experimental tests were conducted by three types of temperature control. It was found that in the case of non-isothermal temperature control with temperature holding was effective for increasing the reactivity of the foam device of ceria. The isothermal experiment for the hercynite and ceria device indicated that the hercynite is capable to release more gas than ceria when compared at the same mass of reactive materials.

Acknowledgments

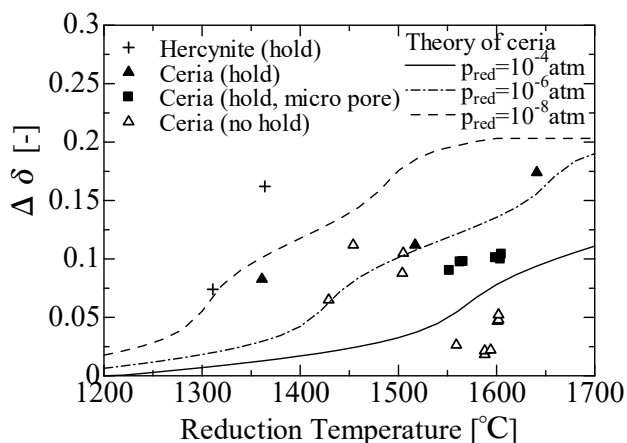Fig.11 Volume of carbon monoxide per mass of material and reaction time.

Fig.12 Change in nonstoichiometry.

4. Conclusion

This study describes the thermochemical splitting of carbon dioxide with ceria and hercynite utilized as redox material. A new facility equipped with the concentrated solar simulator was started up and demonstrated. For the experiments, the foam device of ceria and hercynite was successfully created by the

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