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Hydrogen production in fluidized bed by chemical-looping cycle

Gyoung Tae Jin†, Ho-Jung Ryu, Sung-Ho Jo, Seung-Yong Lee, Sung Real Son* and Sang Done Kim*

Korea Institute of Energy Research, Daejeon 305-343, Korea
*Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
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Abstract−To investigate the feasibility of a chemical-looping hydrogen generation system, we investigated the reduction and water splitting reaction characteristics for three mediators and two reducing gas in a bubbling fluidized bed reactor (0.02 m I.D.). For three oxygen carrier particles (NiO/bentonite, Fe_2O_3/bentonite, (NiO : Fe_2O_3)/bentonite), hydrogen was used as a reduction gas and water was used as an oxidation gas. For (NiO : Fe_2O_3)/bentonite particle, carbon monoxide, which is the main component in the syngas from coal or heavy residue, was used as a reducing gas to check reactivity for the carbon containing fuels and carbon deposition characteristics. Based on the reactivity tests, (NiO : Fe_2O_3)/bentonite particle was selected as the best mediator for the chemical-looping hydrogen generation system to achieve stable continuous operation.

Key words: Chemical-looping Cycle, Hydrogen Production, Inherent CO_2 Capture, Redox, Mediator

INTRODUCTION

Hydrogen is primarily used for chemical applications such as petrochemical processing, production of ammonia and methanol. Moreover, future applications will also include hydrogen as an energy carrier [1,2]. Concerns over the sustainability and environmental impact of our current energy infrastructure have focused on obtaining alternative strategies. In long-term view, the hydrogen will be produced from renewable energy such as solar and wind energy. However, hydrogen from fossil fuels will play a major role until the hydrogen from renewable energy is affordable.

The steam methane reforming (SMR) process is widely used to produce hydrogen in the industrial field [3] and a schematic diagram is shown in Fig. 1. The SMR process consists of feedstock purification, steam reforming, high temperature shift reactor (HTS), low temperature shift reactors (LTS), hydrogen separation, and CO_2 separation by methanation or PSA [4]. There are various hydrogen production processes with methane, such as partial oxidation, thermal dissociation, reforming with CO_2, catalytic partial oxidation, plasma catalytic reforming, and direct cracking. However, most of the conventional processes need hydrogen purification and CO_2 separation processes.

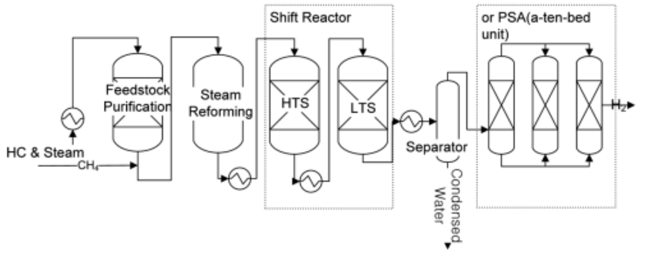

Fig. 1. Typical process configuration of Steam Methane Reforming (SMR) process.

Chemical-looping hydrogen generation system (CLH) is a novel hydrogen production technology with an inherent separation of CO_2. The system consists of two reactors, a water splitting reactor (oxidation reactor) and a reduction reactor. In an oxidation reactor (water splitting reactor), the metal mediator is oxidized by water and hydrogen is produced. Produced gas contains only water vapor and hydrogen. So, high purity hydrogen can be obtained by the condensation of produced gas. The oxidized mediator is transported to a reduction reactor. In the reduction reactor, the mediator reacts with fuel and produces water vapor and CO_2. Highly concentrated CO_2 stream can be obtained by condensation of produced gas from the reduction reactor without any CO_2 separation process and energy penalties. A simplified schematic of a chemical-looping hydrogen

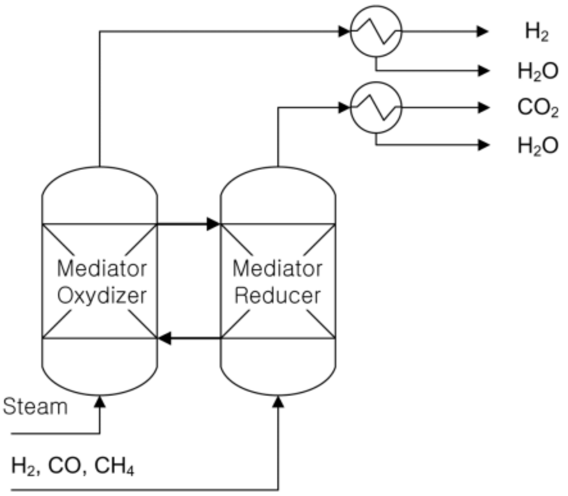

Fig. 2. Simplified schematic of chemical-looping hydrogen generation system.

[†] To whom correspondence should be addressed.
E-mail: gtjin@kier.re.kr

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generator is shown in Fig. 2.

The chemical-looping hydrogen generation system has many advantages. It is very simple because a water gas shift reactor and CO_2 separation process are unnecessary. Moreover, only one kind of particle is required, whereas the conventional steam methane reforming process needs more than four kinds of catalysts/sorbents (catalysts/sorbents for reforming, high temperature water gas shift, low temperature water gas shift, and CO_2 absorption). Most of all, this process can produce highly concentrated hydrogen without any further hydrogen purification process. The chemical-looping hydrogen generation system is very similar to the chemical-looping combustion system [5]. These two systems use metal (or metal oxide) as an oxygen carrier and consist of two interconnected reactors. However, water is used as an oxidizing agent in the chemical-looping hydrogen generator instead of air in the chemical-looping combustor. There are noble concepts to produce hydrogen by chemical cycle. Ryden and Lyngfelt [6] and Zafar et al. [7] introduced a chemical-looping reformer system (CLR). In this system the fuel reactor takes the role of a reformer reactor. Sime et al. [1] proposed and evaluated hydrogen production by REDOX technology. However, some noble concepts need an additional separation process for hydrogen and carbon dioxide.

In the chemical-looping hydrogen generation system, a fuel and a steam go through the different reactors. Eqs. (1)-(4) illustrate the basic concept of the chemical-looping hydrogen generation system. In the reduction reactor, gaseous fuel (CH_4, H_2, CO, C_nH_{2n+2}, or syngas) reacts with metal oxide according to Eqs. (2)-(4), and releases water vapor and carbon dioxide from the top and metal particles (M) from the bottom. The solid products, metal particles, are transported to the water splitting reactor and react with steam, as shown in Eq. (1), and produce hydrogen and metal oxide particles. Metal oxide particles are recycled to the reduction reactor and supply oxygen for the reduction reaction. Between two reactors, metal (or metal oxide) particles play an important role in transportation of oxygen and heat; therefore, the looping material between the two reactors is named as an oxygen carrier particle. Whether a reaction is endothermic or exothermic is dependent on the metal component and fuel. There is an undesirable reaction, carbon deposition, as shown in Eq. (5). By this reaction, carbon deposits on the oxygen carrier particles. However, the carbon deposition can be avoided by control of solid conversion in a continuous two-interconnected reactor system. Moreover, Ryu et al. [8] reported that the carbon-deposition-free operating window can be obtained at low solid conversion and high reaction temperature.

Oxidation reaction by steam:

$$Me+H_2O \rightarrow MeO+H_2 \tag{1}$$

Reducing reaction by fuel:

$$4MeO+CH_4 \rightarrow CO_2+2H_2O+4Me \tag{2}$$

$$MeO+H_2 \rightarrow H_2O+Me \tag{3}$$

$$MeO+CO \rightarrow CO_2+Me \tag{4}$$

Carbon deposition:

$$2CO \rightarrow CO_2+C \tag{5}$$

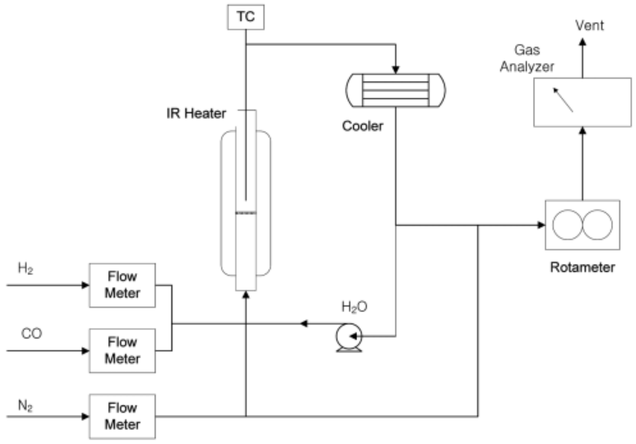

Fig. 3. Schematic of bubbling fluidized bed reactor.

To select the best mediator, some parameters should be considered such as an oxygen carrying capacity (related to solid circulation rate, reactor size, solid inventory, and reaction rate), attrition resistance (related to mediator life span and make-up cost), selectivity (related to additional separation process), and regeneration characteristics (related to efficiency of mediator).

In this paper, reduction and water splitting characteristics of three mediators are investigated in a bubbling fluidized bed reactor. To check reactivity of three mediators without carbon deposition, hydrogen was used as a reducing gas at first. After a reduction test by hydrogen, CO gas was used to investigate reduction characteristics for the syngas.

EXPERIMENTAL

The reactivity tests were carried out in a bubbling fluidized bed reactor. A schematic of the reactor is shown in Fig. 3. The major components consist of a water feeding pump, a gas input system, an IR heater, the fluidization column, a gas cooler, a rotameter, and an on-line gas analyzer. The fluidization column is made of quartz and a sintered porous plate separates a preheating zone and a reaction zone. The preheating zone is 0.2 m high with an internal diameter of 0.02 m and the reaction zone is 0.3 m high with the same internal diameter, so that the total height of the reactor is 0.5 m. Reactant gas was fed to the lower part of the reactor and preheated by the IR heater. The gas flow rate was controlled by mass flow controller and the outlet gas flow rate was checked by rotameter at the outlet of the reactor. Water was fed to the lower zone of the reactor by the water feeding pump and steam was generated by passing through the preheating zone. The exit stream from the fluidized bed reactor was sampled at the outlet of the rotameter. The H_2, CO, and CO_2 concentrations were determined by using an on-line gas analyzer (ABB, Advanced Optima) and recorded by a data acquisition system.

Three kinds of mediators--NiO/bentonite, Fe_2O_3/bentonite, and (NiO : Fe_2O_3)/bentonite--were prepared by physical mixing of metal components and supporter. Prior to the mixing of the metal components and the supporter, the particles were milled in a ball mill for 18 hours. These two powders were mixed (NiO or Fe_2O_3 and bentonite at a ratio of 3 : 2). Distilled water was added to this powder mixture. Obtained paste was dried at 383 K for 24 hours, and calcined at 1,273 K for 6 hours, and crushed. For the dual metal

Table 1. Properties of the three mediators

Name	Composition	Density g/cm^3	Surface area m^2/g
NiO/Bentonite	60% NiO, 40% Bentonite	4.080	2.820
Fe_2O_3/bentonite	60% Fe_2O_3, 40% Bentonite	3.155	1.388
(NiO : Fe_2O_3)/bentonite	30% NiO, 30% Fe_2O_3, 40% Bentonite	3.290	1.940

mediator ((NiO : Fe_2O_3)/bentonite), two metal components, NiO and Fe_2O_3, were mixed at a ratio of 1 : 1. Prior to the start of each experiment, the mediators were sieved to ensure that all particles were initially between 90 and 212 μm in size. The static bed height was about 0.07 m in all cases and this height corresponds to 30 g of mediator; the experiments were carried out batchwise for the mediators; that is, no mediators were added during the run. The properties of three mediators are provided in Table 1.

RESULTS AND DISCUSSIONS

As mentioned before, carbon-containing reducing gases can cause carbon deposition at high solid conversion. However, carbon deposition is a serious problem only in the case of gas-rich conditions such as fixed bed or batch-wise experiment. In the case of solid-rich conditions such as in continuous fluidized bed operation, carbon deposition can be avoided by control of the solid conversion difference between two reactors [8]. When carbon deposits on the mediator, it is difficult to analyze reduction capacity, and therefore hydrogen was used as a reducing gas to avoid the carbon deposition on the mediator at first.

1. NiO/Bentonite Particle

Typical trends of reducing gas conversion and temperature versus time for NiO/bentonite particle during reduction test appear in Fig. 4. In this experiment, a total inlet gas flow was 1.8 N*l*/min (N_2 1.2 N*l*/min, H_2: 0.6 N*l*/min). NiO/bentonite particle shows high reduction gas conversion and it was maintained at 100% up to 7 min and decreased quickly thereafter because of exhaust of oxygen in the particle.

After the reduction test, the particle was subjected to water splitting reaction. Fig. 5 illustrates trends of H_2O conversion and temperature versus time for NiO/bentonite particle during water splitting reaction after full reduction. In this experiment, a total inlet gas flow rate was 2.0 N*l*/min (N_2 1.4 N*l*/min, H_2O 0.6 N*l*/min). The H_2O conversion increased sharply and then decreased abruptly and maintained around 0.8%. As a conclusion, NiO/bentonite particle represented good reduction reactivity and poor water splitting reactivity.

2. Fe_2O_3/Bentonite Particle

As the second mediator, reactivity of Fe_2O_3/bentonite particle was investigated. For the Fe_2O_3/bentonite particle, cyclic tests up to 4*th* cycle were performed at the same flow rate. Fig. 6 illustrates trends of reducing gas conversion versus time. The initial reducing gas conversion was 94% but decreased with time continuously. However, for the 1*st* cycle, reducing gas conversion was higher than that of later cycles and the extent of reduction (cumulative reduction) decreased with increasing number of cycles. From the viewpoint of reduction gas conversion, Fe_2O_3/bentonite particle shows lower reactivity than that of NiO/bentonite particle.

Fig. 7 shows trends of H_2O conversion versus time up to 4*th* cycle.

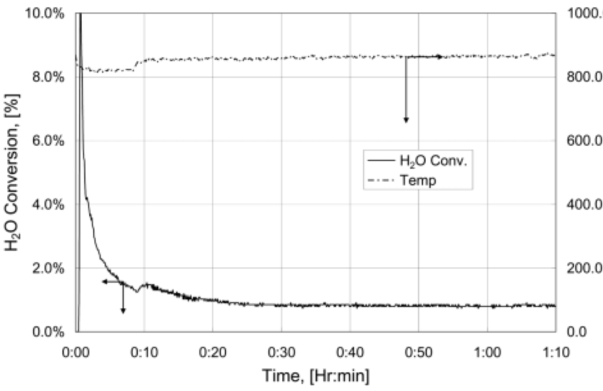

Fig. 5. H_2O conversion vs. time during water splitting reaction of NiO/bentonite particle.

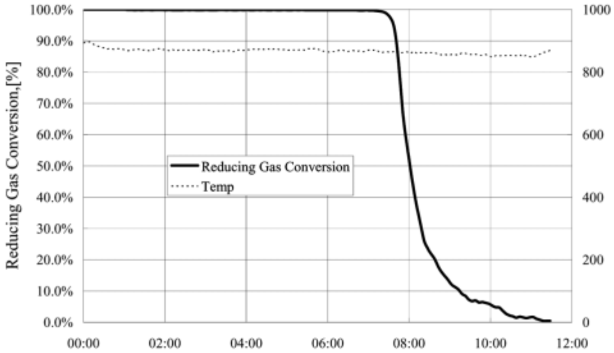

Fig. 4. Reducing gas conversion vs. time during reduction reaction of NiO/bentonite particle.

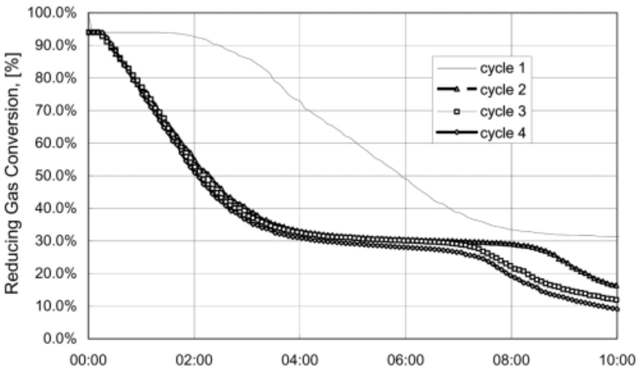

Fig. 6. Reducing gas conversion vs. time during reduction reaction of Fe_2O_3/bentonite particle (T=900 °C).

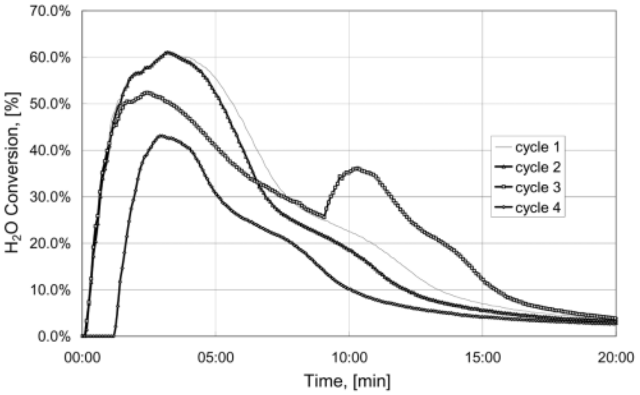

Fig. 7. H_2O conversion vs. time during water splitting reaction of Fe_2O_3/bentonite particle (T=900 °C).

The highest H_2O conversion was about 62% at an initial period of 1^{st} and 2^{nd} cycle. These values are much higher that that of NiO/bentonite particle. However, the effect of cyclic operation was complex. Based on these results, it can be concluded that Fe_2O_3/bneonite particle shows good reactivity for water splitting reaction, but NiO/bentonite particle shows good reactivity for reduction.

3. (NiO : Fe_2O_3)/Bentonite Particle

As mentioned before, NiO/bentonite particle has good reactivity only for the reduction reaction and Fe_2O_3/bentonite particle has good reactivity for the water splitting reaction. To get a synergy effect of these two metal components, we considered a dual metal particle, (NiO : Fe_2O_3)/bentonite, as the third mediator. For the (NiO : Fe_2O_3)/bentonite particle, cyclic tests up to 7^{th} cycle were performed at the same flow rate.

Traces of reducing gas conversions versus time for the (NiO : Fe_2O_3)/bentonite particle for 7 cycles appear in Fig. 8. The reduction gas conversion decreased with time, consistent with Fig. 6 but the trends of the reducing gas conversion were almost same for all cycles and the initial value was 100%. Moreover, the decay of reducing gas conversion with time for (NiO : Fe_2O_3)/bentonite was lower than that of Fe_2O_3/bentonite particle.

Fig. 9 shows trends of H_2O conversion versus time for the (NiO : Fe_2O_3)/bentonite particle for seven cycles. The H_2O conversion increased with time before dropping to 0%. The duration of the water splitting reaction and the total amount of H_2 generation decreased with an increase in the number of cycles. From the viewpoint of stability of water splitting reaction, (NiO : Fe_2O_3)/bentonite particle showed better results than NiO/bentonite and Fe_2O_3/bentonite particle. As a conclusion, (NiO : Fe_2O_3)/bentonite particle was selected as the best mediator for the chemical-looping hydrogen generation system to achieve stable continuous operation.

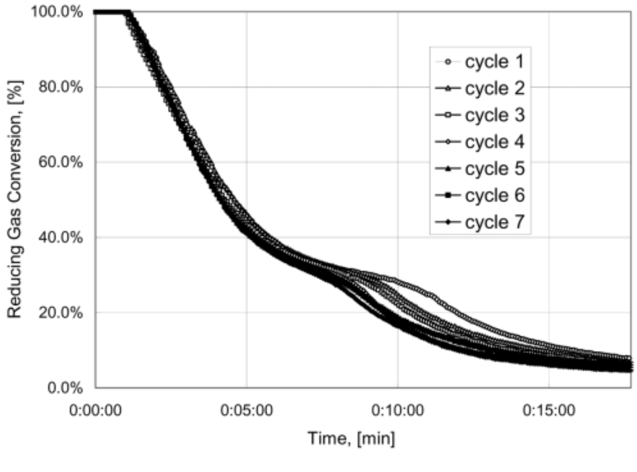

Fig. 8. Reducing gas conversion vs. time during reduction reaction of (NiO : Fe_2O_3)/bentonite particle (T=800 °C).

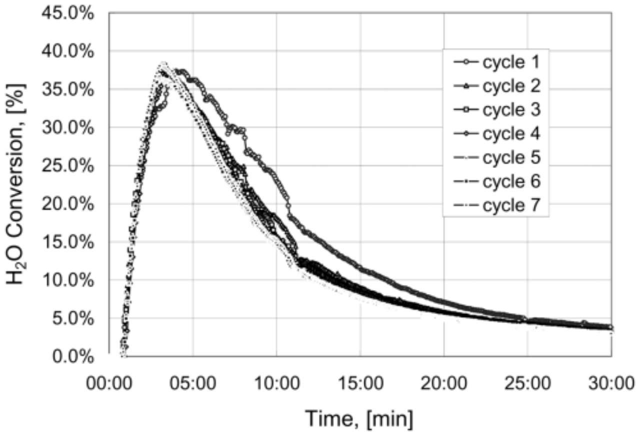

Fig. 9. H_2O conversion vs. time during water splitting reaction of (NiO : Fe_2O_3)/bentonite particle (T=800 °C).

4. Reduction of (NiO : Fe_2O_3)/Bentonite Particle by CO Gas

In the previous tests, hydrogen was used as the reducing gas to prevent carbon deposition. But in a commercial system, carbon-containing fuels such as methane, syngas, and/or natural gas will be used. To check reactivity of the (NiO : Fe_2O_3)/bentonite particle, carbon monoxide, which is the main component in the syngas from coal or heavy residue, was used as the reducing gas. In this experiment, a total inlet gas flow was 1.4 N*l*/min (N_2 1.2 N*l*/min, CO: 0.2 N*l*/min).

Fig. 10 shows trends of CO, CO_2 and CO+CO_2 concentration during reduction of the (NiO : Fe_2O_3)/bentonite particle. At the beginning of the reduction, input CO was partially reacted with oxygen in the mediator and CO_2 concentration increased. After that, con-

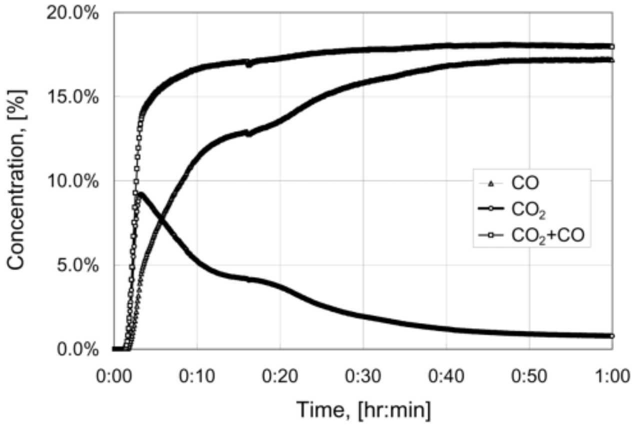

Fig. 10. Exhaust gas composition vs. time during CO reduction of (NiO : Fe_2O_3)/bentonite particle (T=800 °C).

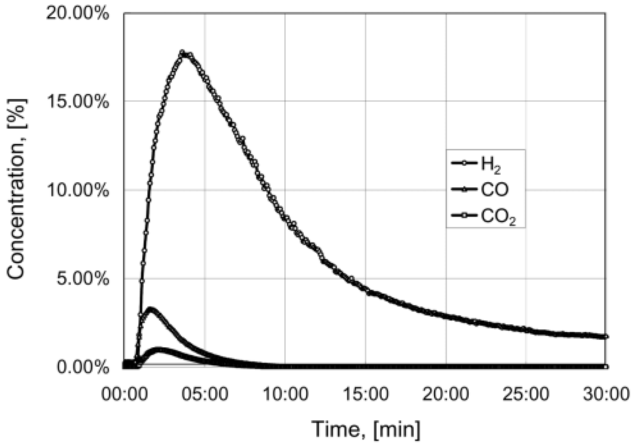

Fig. 11. Exhaust gas composition vs. time during water splitting reaction of (NiO : Fe_2O_3)/bentonite particle (T=800 °C).

centration of CO_2 decreased with time and this means that oxygen in the mediator depleted with time.

After the CO reduction test, the particle was subjected to water splitting reaction. Fig. 11 illustrates trends of H_2O, CO, and CO_2 concentration versus time during water splitting reaction after reduction test. In this experiment, a total inlet gas flow was 1.8 N*l*/min (N_2 1.2 N*l*/min, H_2O: 0.6 N*l*/min). The H_2O concentration increased with time, before dropping slowly to 0%. However, at an initial period, CO and CO_2 were detected. This means that carbon was deposited on the mediator during reduction by CO. The CO and CO_2 were generated from the reaction between the deposited carbon and oxygen in the steam (input water). Ryu et al. [8] reported that carbon deposition can be avoided by control of solid conversion in a continuous two-interconnected reactor system. Moreover, they concluded that carbon deposition does not take place at a low solid conversion range. If we consider the experimental conditions of this study, reduction was performed up to high solid conversion range, and therefore most of the oxygen in the mediator was depleted. In this case, carbon might be deposited by dissociation of CO (Eq. (5)). However, if we operate reduction and water splitting reactor continuously at low solid conversion range, carbon deposition can be avoided, as mentioned in Ryu et al. [8].

CONCLUSIONS

Experiments were performed on reduction and water splitting reaction characteristics for three mediators and two reduction gases in a bubbling fluidized bed. Ni/bentonite particle represented good reduction reactivity and poor water splitting reactivity. However, Fe_2O_3/bentonite particle shows better reactivity for water splitting reaction and poorer reactivity for reduction than NiO/bentonite particle. To get a synergy effect of these two metal components, dual metal particle, (NiO : Fe_2O_3)/bentonite, was investigated as the third mediator. The (NiO : Fe_2O_3)/bentonite particle represented better reduction reactivity than that of Fe_2O_3/bentonite particle and stable water splitting reactivity up to 7^{th} cycle. As a conclusion, (NiO : Fe_2O_3)/bentonite particle was selected as the best mediator for the chemical-looping hydrogen generation system to achieve stable continuous operation. A water splitting reaction test after CO reduction of (NiO : Fe_2O_3)/bentonite particle indicated that carbon was deposited on the mediator during reduction and further research on carbon deposition-free operating window is required to develop a chemical-looping hydrogen generation system with (NiO : Fe_2O_3)/bentonite particle.

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