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Chemical-looping combustion of syngas by means of spray-dried NiO oxygen carrier

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Abstract–Chemical-looping combustion (CLC) of syngas has a potential to generate power economically with achieving the inherent carbon dioxide capture. An oxygen carrier with high reactivity and excellent physical properties would make CLC technology more competitive. In this work, oxygen carrier with 70 wt% NiO was prepared by spray drying technique. The prepared oxygen carrier had excellent physical properties for fluidized-bed application of CLC process. The reactivity of the oxygen carrier in repeated reduction-oxidation was measured by thermogravimetric analyzer with simulated syngas. Oxygen carrier calcined at 1,100 °C showed high oxygen transfer capacity of 14.7 wt%, utilizing 98% of the transferable oxygen. Oxygen transfer capacity and oxygen transfer rate was increased with the increase of reaction temperature, and the highest oxygen transfer rate was observed when about half of the transferable oxygen reacted with syngas. The reduction rate of the syngas (mixture of H_2 and CO) appeared to be approximately the sum of the reaction rate of each fuel gas. The experimental results indicated that the spray-dried NiO oxygen carrier prepared in this work could be a good quality oxygen carrier for the CLC of syngas.

Key words: Oxygen Carrier, Chemical Looping Combustion, Nickel Oxide, Syngas, Carbon Dioxide

INTRODUCTION

Global warming caused by the increase of CO_2 concentrations in the atmosphere is demanding advanced energy technologies emitting less CO_2 while enhancing thermal efficiency. Power generation is one of the largest CO_2 emission sources. In 2006, fossil-fuel power plants emitted 11.4 Gt of CO_2, 41% of world total [1]. Advanced power generation systems with carbon capture and storage (CCS) are expected to contribute to substantial CO_2 emissions reductions. Post-combustion, pre-combustion and oxy-combustion CO_2 capture is being developed for the fossil-fuel power plants. The main application of post-combustion CO_2 capture is pulverized coal (PC) power plants. Pre-combustion CO_2 capture is applicable to integrated gasification combined cycle (IGCC) plants. Oxy-combustion uses gaseous oxygen rather than air to burn fuel resulting in significant reduction of NO_x emission and high CO_2 content in the flue gas.

Chemical-looping combustion (CLC) is one of the most emerging CO_2 capture technologies. CLC combined with IGCC is reported as an innovative CO_2 capture technology with highest cost reduction benefits [2]. A CLC process uses an oxygen carrier composed of metal oxide and support to supply oxygen instead of air or gaseous oxygen for fuel combustion. An oxygen carrier circulates two interconnected fluidized-bed reactors, an air reactor and a fuel reactor, in which oxygen carrier obtains oxygen from the air in the air reactor and transfers the oxygen to fuel in the fuel reactor. Therefore, direct contact between fuel and air is avoided (Fig. 1). The reactions in the fuel reactor for hydrocarbon fuel and syngas are

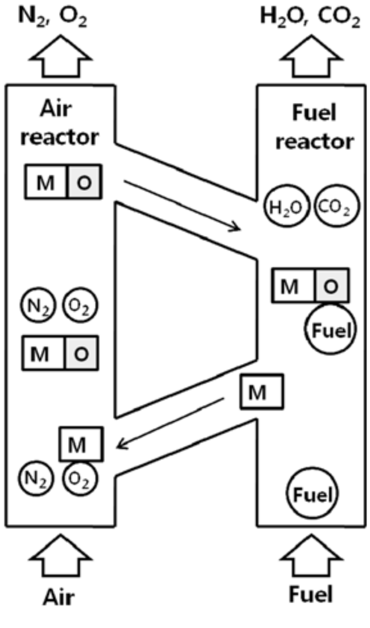

Fig. 1. Schematic drawing of a chemical-looping combustion process (M: metal; O: oxygen).

$$(2n+m)M_xO_y + C_nH_{2m} \rightarrow (2n+m)M_xO_{y-1} + nCO_2 + mH_2O \qquad (1)$$

$$(n+m)M_xO_y + nCO + mH_2 \rightarrow (n+m)M_xO_{y-1} + nCO_2 + mH_2O \qquad (2)$$

and the reaction in air reactor is

$$M_xO_{y-1} + 1/2\ O_2 \rightarrow M_xO_y \qquad (3)$$

where M_xO_y and M_xO_{y-1} denote a metal oxide and a reduced oxide,

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respectively.

Natural gas and syngas from coal gasification are usually considered as fuel in CLC. Recently, direct use of solid fuel in CLC has been studied by some research groups [3-5]. In a CLC system, pure CO_2 can be, in principle, obtained by removing water vapor in the flue gas emitted from the fuel reactor.

The oxygen carrier should have the physical properties and reactivity required for hundreds and thousands of repeated uses in the two fluidized-bed reactors. Sufficient oxygen transfer capacity, high reactivity with fuel and oxygen, high resistance to attrition and agglomeration, long-term durability in reactivity and structural integrity, good physical properties for fluidized-bed process and low production cost are the main criteria for the selection of a quality oxygen carrier. Oxygen carriers in the literature are usually prepared by dry or incipient wetness impregnation method [6-8] or mechanical mixing and extrusion method [9,10]. However, these methods are not adequate for mass production of an oxygen carrier for commercial fluidized-bed application. A research group at Chalmers University in Sweden has been using freeze granulation method to produce a variety of oxygen carriers for lab-scale and pilot-scale CLC process study [11,12]. Recently, they made several oxygen carriers using a spray drying technique [13-16]. A spray drying method is a commercial process to produce various catalysts for fluidized-bed application. It can be readily scaled up to produce large amounts of products. The spray drying method produces particles having highly uniform size and shape.

The KEPCO Research Institute has been using spray drying method to produce regenerable solid CO_2 sorbents and H_2S sorbents for fluidized-bed process. With such advantages mentioned above, we have introduced spray-drying method to develop an oxygen carrier suitable for CLC of syngas. In this work, oxygen carrier with 70 wt% NiO was prepared by spray drying method and its physical properties were characterized. The reactivity tests were performed with thermogravimetric analyzer (TGA). The effect of reaction temperature and fuel type on the reactivity was analyzed in terms of oxygen transfer capacity, oxygen utilization, and oxygen transfer rate.

EXPERIMENTAL SECTION

1. Preparation of the Oxygen Carrier

NiO powder was well-mixed with support materials, which were composed of mainly Al_2O_3, and Al_2O_3-based binder, in pure water where 70 wt% NiO was added on dry basis. During the mixing of inorganic materials, organic dispersant was added to prevent the agglomeration of raw materials. The mixed slurry was comminuted with ball mill to make a homogeneous colloidal slurry. The homogenized slurry was spray-dried to form spherical particles, i.e., green body. The green body was calcined at 1,100 and 1,250 °C in a muffle oven for 3 h after pre-drying at 120 °C overnight.

2. Characterization of the Spray-dried Oxygen Carrier

The morphology of calcined oxygen carrier was obtained using a JEOL JSM 6400 scanning electron microscope (SEM). The sample was coated with gold before the measurements to avoid charging problems. Average particle size of the sample was measured with a MEINZER II sieve shaker based on the American Society for Testing and Materials (ASTM) E-11. Packing density of sample was determined using the Autotap instrument (Quantachrome) according to the ASTM D 4164-88. The packing density was obtained by dividing the known particle mass by its tapped volume. Brunauer-Emmett-Teller (BET) surface area of the sample was determined by N_2 physisorption using an ASAP 2420 (Micromeritics Inc.) automated system. Porosity was obtained from Hg intrusion data using AutoPore IV 9500 (Micromeritics Inc.). The sample was degassed in the system at 100 °C for 4 h and then at 200 °C for 2 h before each measurement.

One of the most important physical properties of oxygen carrier is high resistance to attrition. Attrition resistance of the calcined oxygen carrier was measured with a modified three-hole air-jet attrition tester based on the ASTM D 5757-95. The attrition resistance was determined at 10 slpm over 5 h as described in the ASTM method. The attrition index (AI) is the percent fines generated over 5 h. The fines are particles less than 40 μm collected at the thimble after 5 h from the start, which was attached to the gas outlet.

$$\text{AI}=[\text{total fine collected for 5 h/amount of initial sample (50 g)}]\times 100\% \tag{4}$$

A lower AI indicates a better attrition resistance of the bulk particles. The AIs of fresh Akzo and Davison fluid catalytic cracking (FCC) catalysts as the reference were 22.5% and 18.4%, respectively, under the same measurement condition. A little higher value of AI than those of commercial FCC catalysts could be acceptable because an oxygen carrier in CLC is circulated in a less severe condition relative to FCC process. The superficial gas velocity of FCC process is around two times higher than that of the CLC process.

3. TGA Chemical Reactivity of the Spray-dried Oxygen Carrier

Reduction and oxidation reactivity of spray-dried NiO oxygen carrier was investigated using a TGA (Thermo Cahn, TherMax500) at the reaction temperatures of 700-1,000 °C. A simulated syngas was used as reducing gas and air was used as oxidizing gas. After each reduction and oxidation period, the reactor was purged with N_2 gas to avoid mixing of fuel and air. The gas flow rate of 150 ml/min (STP) was used for all periods. A 20 mg of oxygen carrier was loaded in an alumina crucible and heated to the specified reaction temperature under nitrogen atmosphere at ambient pressure. After the balance of TGA was stabilized, repeated reduction and oxidation tests were carried out for the oxygen carrier by alternating syngas and air. At least five iterative tests were performed with each oxygen carrier to obtain the stabilized oxygen transfer capacity and reactivity data after several times of cyclic redox reaction. Data from the fifth cycle were used for the analysis of oxygen transfer rate.

4. Analysis of TGA Reactivity Data

The reactivity of the oxygen carrier was analyzed in the terms of the oxygen transfer capacity and the oxygen transfer rate. Oxygen transfer capacity is the maximum percentage of mass change by oxygen transfer under the given experimental conditions and it is calculated on the basis of the mass of the fresh oxygen carrier in its fully-oxidized state. The degree of conversion, X, of a metal oxide is defined as:

$$X=\frac{m_{ox}-m}{m_{ox}-m_{red}} \tag{5}$$

where m is the instantaneous mass of an oxygen carrier measured by TGA, and m_{ox} and m_{red} are the theoretical masses of the oxygen carrier in its fully-oxidized and fully-reduced state, respectively, when it is assumed that all oxygen present in the NiO which was added as a raw material is transferrable. The m_{ox} is equal to the mass of the fresh oxygen carrier in its fully-oxidized state. The denominator of Eq. (5), the weight difference between m_{ox} and m_{red}, is the theoretical maximum amount of oxygen that can be transferred to the fuel. Oxygen utilization is percentage of the degree of conversion during the reduction reaction. The oxygen transfer rate is expressed as the mol of transferred oxygen per unit gram of oxygen carrier per unit time (mol O/g_{oc}/s).

The oxygen ratio of the oxygen carrier, R_o, is the theoretical maximum mass fraction of oxygen that can be transferred to fuel. R_o is defined as;

$$R_o=(m_{ox}-m_{red})/m_{ox} \tag{6}$$

The value of R_o of pure NiO is 0.214. The value of R_o of spray-dried oxygen carrier in this study can be calculated from the NiO content, 70 wt%, of the prepared sample and the corresponding R_o is 0.150 (15.0%).

A mass-based conversion, ω, was used to compare the amount of mass change as a function of time as defined;

$$\omega=\frac{m}{m_{ox}}=1+R_o(X-1) \tag{7}$$

Accordingly, the theoretical mass-based conversion (ω) of the prepared sample at its fully reduced state should be 0.853 on a dry solid raw material basis.

RESULTS AND DISCUSSION

1. Physical Characterization of the Spray-dried Oxygen Carrier

The shape of the spray-dried oxygen carrier and the surface morphology are shown in Fig. 2. Most particles of the prepared oxygen carrier were spherical. The morphology magnified by 5,000 times ((b) and (d) in Fig. 2) showed that most of the solid raw materials were ground into grains below 2 μm. The sphericity of the particles in this work was remarkably improved compared with previously reported spray-dried oxygen carriers [14,15,17] of which a large fraction showed donut or dimple shape. The spherical shape will contribute to the reduction of attrition loss by rounding effect.

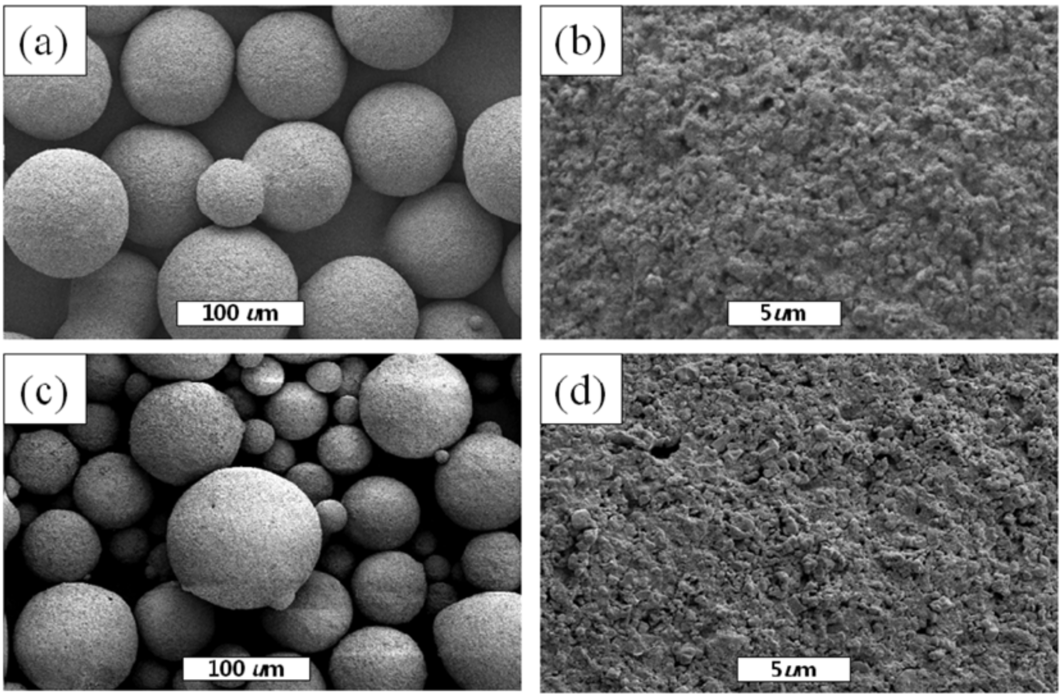

Fig. 2. SEM images of the spray-dried oxygen carrier: ((a) and (b)) oxygen carrier calcined at 1,100 °C; ((c) and (d)) oxygen carrier calcined at 1,250 °C.

Table 1. Physical properties of the spray-dried oxygen carriers

Calcination temperature /°C	Average particle size /μm	Tapped density /(g/ml)	Surface area/(m^2/g)					Pore volume/(ml/g)				Porosity[b] /%	Attrition index (AI) /%
			BET	Total[c]	Micro-pore[a]	Meso-pore[b]	Macro-pore[b]	Total	Micro-pore[a]	Meso-pore[b]	Macro-pore[b]		
1100	82	1.63	15.3	16.52	3.05	10.88	5.64	0.19	0.0013	0.066	0.12	26.8	28.9
1250	76	2.00	3.2	5.04	2.21	0.95	4.09	0.13	0.0009	0.0069	0.12	21.8	12.0

[a] Calculated using the t-plot method for N_2 adsorption isotherm

[b] Calculated from Hg intrusion data

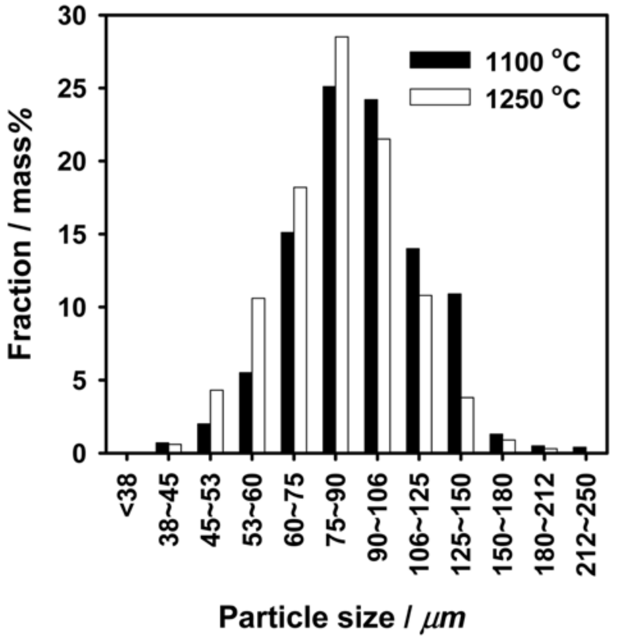

Fig. 3. Particle size distribution of NiO-based oxygen carrier prepared by spray drying method.

Other physical properties of the prepared oxygen carrier are summarized in Table 1. Average particle sizes (82 and 76 μm) and packing densities (1.63 and 2.01 g/cm^3) are suitable for fluidized-bed applications. Around 99 wt% of both samples fell in the particle size range of 38 to 212 μm as shown in Fig. 3. A particle size range of 50 to 400 μm is suitable for fluidized-bed reactors such as bubbling, circulating, fast- and transport-type reactors [18,19]. The particle size of typical FCC catalysts ranges from 40 to 150 μm with an average particle size of about 80 μm [19]. Higher packing density at 1,250 °C is due to the smaller particle size by contraction of body at the higher calcination temperature. Specific surface area was remarkably reduced from 15.3 to 3.2 m^2/g, while porosity reduction was not significant with the increase of the calcination temperature from 1,100 to 1,250 °C. This implies that the most of small pore (micropore and mesopore) was destroyed, but large pore (macropore) was maintained its structure during higher temperature calcination (1,250 °C). The pore volume and surface area by pore size given in Table 1 support this estimation. Although the surface area decreased when the calcination temperature increased to 1,250 °C, it is still higher than the previously reported spray-dried oxygen carriers [15, 16].

The AI of the spray-dried oxygen carrier is below 30%, indicating good mechanical strength of solid particles which are suitable to a fluidized-bed CLC process. The mechanical strength of the spray dried sample was improved from 28.9% to 12% as the calcination temperature increased from 1,100 to 1,250 °C. It suggests that a calcination temperature between 1,100 °C and 1,250 °C is desirable to obtain sufficient mechanical strength for the spray-dried oxygen carrier prepared in this work.

2. TGA Reactivity

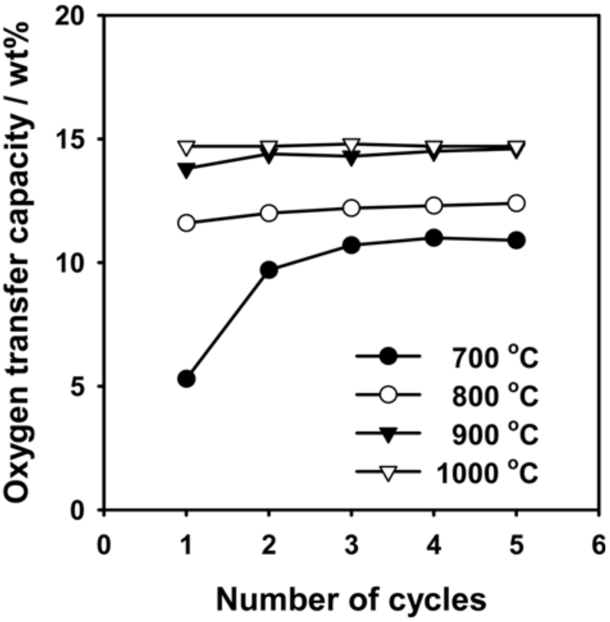

Fig. 4. Typical effect of temperature on the oxygen transfer capacity as a function of the number of cycles during reduction period of spray-dried NiO oxygen carrier calcined at 1,100 °C, using syngas as a fuel.

The results of the multicycle oxygen transfer capacity of the spray-dried oxygen carrier calcined at 1,100 °C are shown in Fig. 4. The composition of simulated syngas was 28.7 vol% H_2, 41 vol% CO, 12.3 vol% CO_2, and 18 vol% N_2. At the higher reaction temperatures, the oxygen transfer capacity was stabilized in the earlier redox cycle test. At 1,000 °C, the oxygen transfer capacity reached its maximum value from the first cycle test and it was maintained in the later cycle tests. However, the oxygen transfer capacity at 700 and 800 °C was stabilized from the third cycle test. The oxygen transfer capacity of reduction reaction increased with the increase of reaction temperature. At 900 and 1,000 °C, the oxygen transfer capacity reached 14.7 wt%, utilizing 98% of the transferable oxygen. The oxygen transfer capacity was 12.4 wt% at 800 °C, corresponding to the oxygen utilization of 83%. It was decreased to 10.9 wt% at 700 °C, or oxygen utilization of 73%. The high oxygen utilization of around 98% means that NiO was well dispersed in the spray-dried oxygen carrier and the prepared oxygen carrier had excellent textural properties for the diffusion of reactant gases and product gases. High oxygen transfer capacity and high oxygen utilization will contribute to the reduction of the oxygen carrier inventory, circulation rate and process operating cost. The oxygen utilization of the oxygen carrier prepared in this work was higher than that of previously reported spray dried NiO oxygen carrier, which was prepared with the raw materials mixed with α-Al_2O_3 and NiO to give an active NiO content of 40% [13]. The high oxygen utilization in this work could be achieved by the improved physical properties and the increased free NiO content, which resulted from the use of γ-Al_2O_3 as a main raw support material and the higher initial NiO content. The effect of the use of γ-Al_2O_3 and NiO content on the performance of the spray-dried NiO oxygen carriers was well described in our previous study [20].

A five-cycle test result for the oxygen carrier calcined at 1,250 °C, which is not shown here, also showed excellent oxygen transfer capacity of 14.4 wt% at the reaction temperature of 950 °C, although its specific surface area is only about 20% compared to that of the

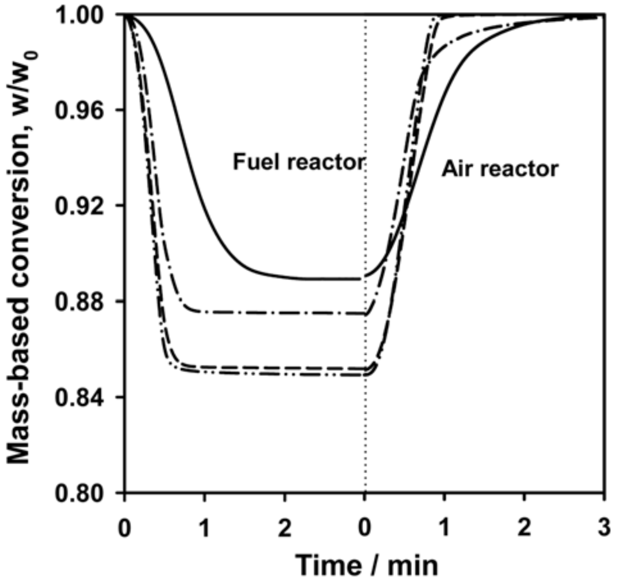

Fig. 5. Typical effect of reaction temperature on the mass-based conversion as a function of reaction time for the spray-dried NiO oxygen carrier calcined at 1,100 °C. A simulated syngas (28.7 vol% H_2, 41 vol% CO, 12.3 vol% CO_2, and 18 vol% N_2) and air were used as a fuel and an oxidizing gas, respectively.

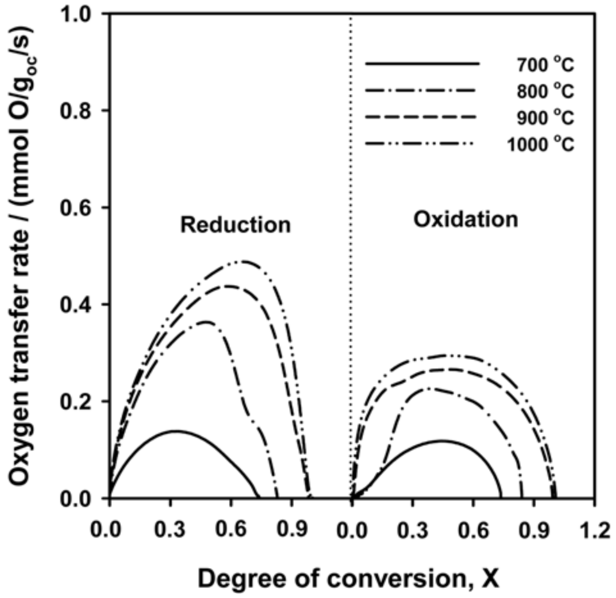

Fig. 6. Typical effect of temperature on the oxygen transfer rate as a function of degree of conversion for the spray-dried NiO oxygen carrier calcined at 1,100 °C. A simulated syngas (28.7 vol% H_2, 41 vol% CO, 12.3 vol% CO_2, and 18 vol% N_2) and air were used as a fuel and an oxidizing gas, respectively.

oxygen carrier calcined at 1,100 °C. Despite the marked reduction of the surface area, the oxygen carrier calcined at 1,250 °C showed similar reactivity to that of the oxygen carrier calcined at 1,100 °C. It indicates that the prepared oxygen carrier maintains its excellent textural properties up to the calcination temperature of 1,250 °C. Cycle test results showed that the prepared spray-dried oxygen carrier had high oxygen transfer capacity and oxygen utilization at the reaction temperature of 900-1,000 °C.

Mass-based conversion of reduction and oxidation at different temperatures is shown in Fig. 5. Reduction and oxidation of oxygen carrier were completed within 2 min at 700-1,000 °C. The oxygen carrier reacted more rapidly with syngas and air at the higher temperatures. After 1 min of reaction, reduction and oxidation progressed 97.8 and 99.8%, respectively, for the 1,000 °C cycle test, while only 43.9 and 64.5% for the 700 °C cycle test. During five cycle redox tests, spray-dried NiO oxygen carrier was almost completely oxidized to its initial state after the oxidation period. It is important that an oxygen carrier must have a good regenerability for repeated cyclic uses. Similar results on the increase of oxygen transfer capacity and conversion with the increase of temperature in CLC of syngas by a NiO based oxygen carrier were reported in the Siriwardane et al.'s study [10]. They used an oxygen carrier with 60 wt% NiO supported on bentonite, which was prepared by simply mixing of raw materials with deionized water followed by calcination at 900 °C and crushing. They reported the oxygen utilization of 56-64% at the reaction temperatures of 700-900 °C, which is less than that of the spray-dried oxygen carrier prepared in this study.

Meanwhile, carbon deposition was observed during the reduction at the reaction temperature of 700 °C, which is not shown in Fig. 5, because syngas was switched to nitrogen right after the mass increase by carbon deposition was observed. The mass of oxygen carrier increased only after oxygen utilization approached to about 73%. The deposited carbon was easily oxidized when air was introduced to the oxygen carrier. The carbon deposition, however, was not observed at the reaction temperature above 800 °C. Ryu et al. [21,22] reported similar results for the NiO/bentonite oxygen carrier prepared by mechanical mixing. In their reactivity tests using CH_4 as a fuel gas, the carbon deposition decreased with the increase of reaction temperature and it was not observed at the reaction temperatures above 900 °C.

Deposited carbon could swell the oxygen carrier resulting in fracture, and it also could reduce the oxygen transfer capacity and reactivity. Therefore, the temperatures without carbon deposition should be used for CLC process.

The rates of reduction and oxidation of the spray-dried oxygen carrier are depicted in Fig. 6 as a function of degree of conversion. The reaction rate of the oxygen carrier varied greatly with the change of degree of conversion and reaction temperatures. The redox reaction was slow at the beginning and the end stages. Maximum oxygen transfer rate at 1,000 °C was around three times higher than that at 700 °C in both reduction and oxidation. The highest reaction rate at each temperature was observed when the degree of conversion approached to around a half of its maximum value. This indicates that the best performance of CLC could be obtained when the oxygen carrier in the fuel reactor and the air reactor is controlled in the vicinity of a half reduced state compared to its fully reduced state. Ishida et al. [17] also reported the reactivity at 900 °C for spray-dried NiO oxygen carrier with average diameter 97 μm which was composed of 60 wt% NiO and 40 wt% $NiAl_2O_4$ and calcined at 1,300 °C. They used more than 70 wt% NiO derived from $Ni(NO_3)_2 \cdot 6H_2O$ to take into account the formation of $NiAl_2O_4$ during calcination by the interaction between NiO and Al_2O_3, resulting in spray-dried oxygen carrier with the weight ratio of NiO to $NiAl_2O_4$ as 6 : 4. Their TGA curve for reduction and oxidation had similar pattern to the ones in this study. They presented the reaction rate as the variation of degree of conversion per unit time (dX/dt). Absolute values of the rate of reduction and the rate of oxidation by Ishida et al. [17] were $4.8\times10^{-2}\ s^{-1}$ with 100% H_2 and $1.9\times10^{-2}\ s^{-1}$ with air, respectively. The oxygen carrier calcined at 1,250 °C in this work exhibits the reduction rate of $9.53\times10^{-2}\ s^{-1}$ with 100% H_2 and $2.79\times10^{-2}\ s^{-1}$ with syngas, and the oxidation rate of $2.55\times10^{-2}\ s^{-1}$ with air. The higher reaction rate in this work indicates again that the prepared oxygen carrier has excellent NiO dispersion and textural properties.

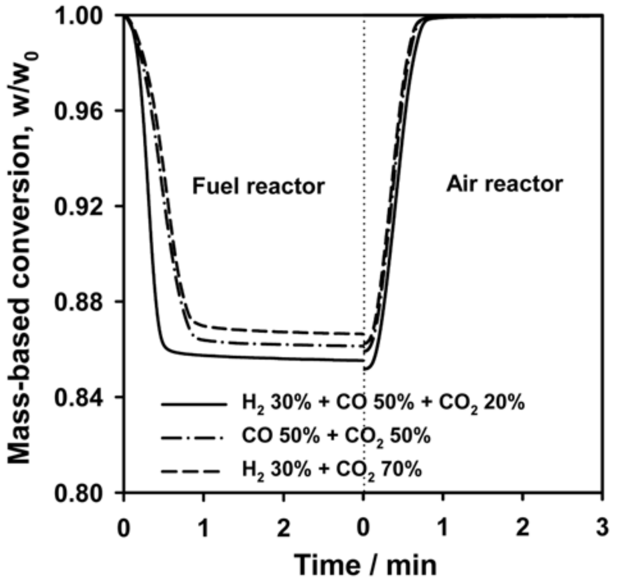

Fig. 7. Typical effect of gas composition on the mass-based conversion as a function of reaction time at the reaction temperature of 950 °C for the spray-dried NiO oxygen carrier calcined at 1,100 °C.

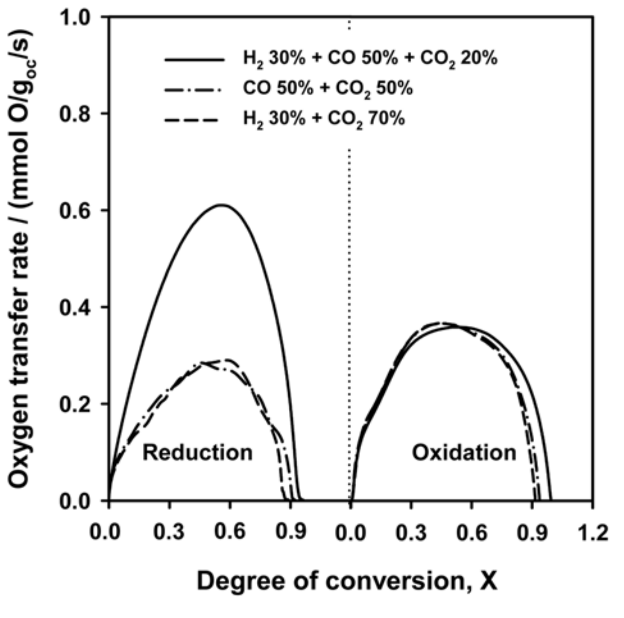

Fig. 8. Typical effect of gas composition on the oxygen transfer rate as a function of degree of conversion at the reaction temperature of 950 °C for the spray-dried NiO oxygen carrier calcined at 1,100 °C.

Maximum degree of conversion at each reaction temperature is also found in Fig. 6. The maximum degree of conversion at the reaction temperatures of 900 and 1,000 °C approached 1.0, which indicates almost all the oxygen in the NiO added as raw material was transferred to syngas.

The effects of fuel type on the reactivity are given in Figs. 7 and 8. At a higher fuel concentration, a little higher oxygen transfer capacity and oxygen utilization can be observed. The oxygen transfer rate during reduction with the simulated syngas (H_2 30 vol%, CO 50 vol%, and CO_2 20 vol%) was approximately the sum of the oxygen transfer rate of each fuel gas (Fig. 8). The reaction rate during oxidation was similar regardless of fuel type because the same oxidizing gas (air) was used.

CONCLUSIONS

The oxygen carrier with 70 wt% NiO was prepared by spray drying method and the CLC of simulated syngas was conducted at the reaction temperatures of 700-1,000 °C under atmospheric pressure. The spray-dried oxygen carrier developed here showed excellent physical properties such as spherical shape, high mechanical strength, macroporous structure, etc., suitable for the fluidized-bed reactors of a CLC process.

With the increase of the reaction temperature, the oxygen transfer capacity and the reaction rate increased. At the reaction temperatures above 900 °C, more than 98% of the oxygen in the NiO used as a raw material for the oxygen carrier preparation was transferred to syngas, and the reduced oxygen carrier regenerated to its initial oxidized state by oxidation with air. The oxygen transfer rate reached its maximum value when the oxygen carrier was reduced to around half of its fully reduced state. It was observed that the oxygen transfer rate during reduction for the fuel (mixture of H_2 and CO) was approximately the sum of the oxygen transfer rate of each fuel gas.

This work showed that an oxygen carrier with high NiO content, excellent physical properties, and high reactivity can be prepared by spray drying method. From the experimental results, it can be concluded that the oxygen carrier prepared in this work could be a quality oxygen carrier for the CLC of syngas. In our future works, a spray-dried NiO oxygen carrier with improved physical properties and reactivity will be developed and more detailed reactivity tests will be conducted in a fluidized-bed reactor.

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NOMENCLATURE

Symbol

X : degree of conversion

m : mass of oxygen carrier [g]
m_{ox} : mass of oxygen carrier in its fully oxidized state [g]
m_{red} : mass of oxygen carrier in its fully reduced state [g]
R_o : theoretical maximum mass fraction of transferable oxygen

Greek Symbol

ω : mass-based conversion

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