Cyclic Reduction and Oxidation Characteristics of Four Oxygen Carrier Particles for Chemical-looping Combustion

Ho-Jung Ryu, Dal-Hee Bae, Young Cheol Park, Seung-Yong Lee
Korea Institute of Energy Research, Daejeon 305-343, Korea
hjryu@kier.re.kr

Abstract

Cyclic reduction and oxidation characteristics of four oxygen carrier particles by using syngas as fuel have been investigated. Experiments were performed in a fluidized bed reactor. All four oxygen carrier particles showed high gas conversion, high CO$_2$ selectivity, and low CO concentration in the reducer and very low NOx (NO, NO$_2$, N$_2$O) emissions in the oxidizer. Moreover, all particles showed good regeneration ability during successive reduction-oxidation cyclic tests up to the 10$^{th}$ cycle. The results indicate that inherent CO$_2$ separation, NOx-free combustion, and long-term operation without reactivity decay of oxygen carrier particles are possible in the syngas fueled chemical-looping combustion system with NiO/bentonite, NiO/NiAl$_2$O$_4$, Co$_x$O$_y$/CoAl$_2$O$_4$, and OCN-650 particles. However, Co$_x$O$_y$/CoAl$_2$O$_4$ represented slightly decay of oxidation reactivity with the number of cycles increased and the oxidation rate was slower than other particles.

Introduction

Carbon dioxide, a major greenhouse gas, is produced in large quantities from combustion of fossil fuels, much of this related to electric power generation. In a conventional power generation system, fuel and air are directly mixed and burned; therefore it is not easy to separate CO$_2$ from flue gas because CO$_2$ is diluted by N$_2$ in air. Chemical-looping combustion (CLC) is a novel combustion technology with inherent separation of the greenhouse gas CO$_2$ and low NOx emission.

The previous results on chemical-looping combustion technology have concentrated on improvement of the oxygen carrier particles and most of the studies used methane or hydrogen as a reduction gas [1]. In order to understand the performance and the feasibility of the chemical-looping combustion system, it is necessary to check the performance of the oxygen carrier particles by using gaseous fuel such as natural gas and syngas. Moreover, confirmation of reduction of NOx emission in the oxidizer and high CO$_2$ selectivity in the reducer are prerequisite for application of the chemical-looping combustion system in commercial plants.

There are many reports on the reactivity of oxygen carriers for a chemical-looping combustor, but most of the previous works were performed with a TGA or fixed bed reactor and the data of gas concentrations from oxidizer and reducer were infrequent. Moreover, there is no report on NOx emissions during oxidation at all. Adanez et al. [2] used a TGA for reaction tests, and there is no data on gas concentration during reduction and oxidation. Corbella et al. [3] used a fixed bed reactor, but they measured gas concentration with a TPR. In their report, gas concentrations were plotted with an arbitrary unit and quantitative analyses of gas conversion and CO$_2$ selectivity were not provided. Diego et al. [4] used a fluidized bed reactor, and they
reported the product gas distribution, but the effect of the number of cycles on the product gas distribution was provided only for CO₂ concentration. Moreover, Diego et al. [4] did not measure the NOx concentration during oxidation. Recently, Ryu et al. [5] reported natural gas combustion characteristics of three oxygen carriers in a fluidized bed reactor. In their report, CO₂ selectivity, NOx concentration data were provided.

Natural gas has been considered as a major fuel in the chemical-looping combustor so far. However, syngas has lately attracted considerable attention as a fuel can substitute for natural gas in the chemical-looping combustor because of high oil price. However, there is a lack of experimental data on syngas-fueled chemical-looping combustion. Mattison et al. [6] used a TGA and a batch fluidized bed for syngas combustion tests, but the effect of temperature on the product gas distribution was provided only for CO concentration. Johansson et al. [7] used a fluidized bed reactor for syngas combustion tests, and they reported the product gas distribution, but did not measure the NOx concentration during oxidation.

In this study, syngas combustion characteristics of oxygen carrier particles were investigated in a batch type fluidized bed reactor (0.05 m ID, 0.7 m high). Four particles, NiO/bentonite, NiO/NiAl₂O₄, CoₓOᵧ/CoAl₂O₄, OCN-650 were used as oxygen carrier particles. Simulated syngas and air were used as reactants for reduction and oxidation, respectively. To check feasibility of good performance, inherent CO₂ separation, and low-NOx emissions, CH₄, CO, CO₂, O₂, H₂, NO, NO₂, N₂O concentrations were measured by on-line gas analyzer. Moreover, the regeneration ability of the oxygen carrier particles was investigated by successive reduction–oxidation cyclic tests up to the 10th cycle.

**Experimental**

Multi-cycle tests were carried out in a bubbling fluidized bed reactor. A schematic of the reactor is shown in Fig. 1. The major components consist of a gas input system, the fluidization column, a hot gas filter, a condenser, a gas cooler, and a gas sampling/analyzing unit. The fluidization column is 0.7 m high with an internal diameter of 0.05 m. A perforated gas distributor plate separates the fluidization column and the air box. Reactant gas was fed to the air box. An electric heater could be controlled by a thermocouple and a heater controller. Thermocouple measurements of temperature and pressure transducer data were recorded by a data acquisition system. The exit stream from the fluidized bed reactor was sampled at the outlet of the reactor. The CH₄, CO, CO₂, H₂, NO, NO₂, N₂O, and O₂ concentrations were determined using an on-line gas analyzer and recorded by the data acquisition system. Further details of the reactor system are available elsewhere [8].

The four oxygen carrier particles tested were NiO/bentonite, NiO/NiAl₂O₄, CoₓOᵧ/CoAl₂O₄, and OCN-650. For economical operation of the chemical-looping combustor, the cost of the oxygen carrier is a very important factor. However, most of the previous researchers used oxygen carriers made of expensive chemical-grade raw materials because they produced only a small amount of carriers for tests in the TGA, fixed bed, and small scale fluidized bed. If we want to operate a larger plant to demonstrate continuous long-term operation of the chemical-looping combustor, mass production of carriers is prerequisite and cheaper raw materials will be helpful to save make-up costs of carriers and operating costs of the chemical-looping combustor. In this study, NiO/bentonite particles were made of commercial-grade raw materials. The cost of raw materials is less than 65% of other carriers. We also used NiO/NiAl₂O₃ and CoₓOᵧ/CoAl₂O₄ particles made of chemical-grade raw materials for comparison with NiO/bentonite particles. Moreover, OCN-650 particles were produced by spray-drying method and have spherical shape.
In our previous works [8-13], many kinds of oxygen carrier particles such as NiO/bentonite, NiO/NiAl2O4, Co3O4/CoAl2O4, (NiO+Fe)/bentonite, NiO/YSZ, (NiO+Fe)/YSZ, NiO/hexaaluminate, Co3O4/hexaaluminate, OCN-650 were developed and reactivity and attrition resistance of carriers were tested by using TGA, fluidized bed and ASTM attrition tester (D5757-95). Based on the previous results, we selected those four carriers as candidates. Prior to the start of each experiment, the oxygen carrier particle was sieved to ensure that all particles were initially between 106 and 212 µm in size. The static bed height was 0.4 m in all cases, and the experiments were carried out batchwise for the particles, i.e. no particles were added during the run. The fluidized bed reactor operated with a total inlet gas flow of 2.0 Nl/min in all cases, corresponding to superficial gas velocities of 0.07 m/s at 900°C. Particles were oxidized in air as the bed temperature was increased from room temperature to 900°C. Once the particle was fully oxidized, the particle was exposed to a gas mixture. The gas mixture contained 45% syngas and 55% N2 for all reduction tests. The inlet concentrations were measured by bypassing the reactor. In this study, we selected the composition of the simulated syngas as H2:CO2:CO=30:10:60, to simulate syngas from coal gasifier of Shell and Texaco (Shell: H2 : CO2 : CO = 31.6 : 0.8 : 64.0; Texaco: H2 : CO2 : CO = 27.8 : 12.5 : 40.0) [14]. Between the cyclic oxidation and reduction tests, nitrogen was used as a purge gas. A rapid decrease in the exit gas concentration marked the end of purge. For each particle, ten cycles of reduction–oxidation were carried out. The properties and preparation methods of four oxygen carriers and experimental conditions are summarized in Tables 1 and 2, respectively.

Table 1. Properties and preparation methods of four oxygen carrier particles

<table>
<thead>
<tr>
<th>Oxygen carrier particles</th>
<th>NiO/bentonite</th>
<th>NiO/NiAl2O4</th>
<th>Co3O4/CoAl2O4</th>
<th>OCN-650</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size range [µm]</td>
<td>106-212</td>
<td>106-212</td>
<td>106-212</td>
<td>106-212</td>
</tr>
<tr>
<td>Metal oxide wt.%</td>
<td>60</td>
<td>70</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Bulk density [kg/m³]</td>
<td>1172</td>
<td>1520</td>
<td>1024</td>
<td>903</td>
</tr>
<tr>
<td>Preparation methods</td>
<td>Mixing</td>
<td>Dissolution</td>
<td>Coprecipitation/Impregnation</td>
<td>Spray drying</td>
</tr>
</tbody>
</table>
Table 2 Summary of experimental conditions

<table>
<thead>
<tr>
<th>Variables</th>
<th>NiO/bentonite, NiO/NiAl2O4, CoOx/CoAl2O4, OCN-650</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static bed height [m]</td>
<td>0.4</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>900, Isothermal</td>
</tr>
<tr>
<td>Method</td>
<td>(Red./Pur./Oxi./Pur. = 10/10/30/10min) × 10 cycles</td>
</tr>
<tr>
<td>Purge gas</td>
<td>N2 (2.0 l/min)</td>
</tr>
<tr>
<td>Reactant gas (reduction)</td>
<td>Simulated syngas (0.89 l/min) + N2 (1.11 l/min)</td>
</tr>
<tr>
<td>Reactant gas (oxidation)</td>
<td>Air (2.0 l/min)</td>
</tr>
</tbody>
</table>

Results and Discussion

The effects of reduction–oxidation cycling on the fuel conversion of four oxygen carrier particles during reduction are shown in Fig. 2. The fuel conversion is defined as (moles of reacted fuel)/(moles of input fuel). The moles of reacted fuel are calculated by measured CO and CO2 concentration. The input fuel concentration was measured before each cycle by bypassing the reactor. The fuel conversions for NiO/bentonite, NiO/NiAl2O4, and OCN-650 particles increased slightly with the number of cycles. We suppose that the internal pore structure can be changed during successive reduction and oxidation cycles at 900°C. We measured the porosity of fresh carriers and particles after the 10th cycle test by mercury porosimeter. The porosity of those three particles after the 10th cycle was slightly higher than that of fresh particles but the porosity of CoOx/CoAl2O4 particle decreased after cyclic test. The average values of fuel conversion during ten cycles for NiO/bentonite, NiO/NiAl2O4, CoOx/CoAl2O4, and OCN-650 particles were very high, the values being 99.5, 99.6, 100, 99.3%, respectively.

![Graph showing fuel conversion vs. number of cycles](image)

Fig. 2. Fuel conversion vs. number of cycles

The effects of reduction–oxidation cycling on the CO2 selectivity of four oxygen carrier particles during reduction are shown in Fig. 3. CO2 selectivity indicates the portion of CO2 per carbon in consumed fuel ([CO2]/[Carbon in consumed fuel]). The CO2 selectivity for NiO/bentonite, NiO/NiAl2O4, and OCN-650 particles slightly increased with the number of cycles, consistent with Fig. 2. The average values of CO2 selectivity during ten cycles for
NiO/bentonite, NiO/NiAl$_2$O$_4$, Co$_x$O$_y$/CoAl$_2$O$_4$, and OCN-650 particles were very high and the values were 99.3, 99.4, 100, 98.9%, respectively.

Fig. 3. CO$_2$ selectivity vs. number of cycles.

Fig. 4(a) and (b) represents hydrogen concentration during reduction and NOx concentration during oxidation, respectively. Hydrogen was not detected at all for all four particles as shown in Figure 4(a). This result indicates that all of hydrogen in the syngas was converted to water. Moreover, NO, NO$_2$, and N$_2$O were not detected for all cycles and for all particles as shown in Figure 4(b). Based on the results, we could conclude that NOx-free combustion is realizable in the syngas fueled chemical-looping combustion system with NiO/bentonite, NiO/NiAl$_2$O$_4$, Co$_x$O$_y$/CoAl$_2$O$_4$, and OCN-650 particles.

Fig. 4. (a) H$_2$ concentration vs. number of cycles and (b) NOx concentration vs. number of cycles.
Fig. 5 shows O₂ concentration profile during successive oxidation reaction up to the 10th cycle. All four particles represented good regeneration ability during oxidation. However, CoₓOᵧ/CoAl₂O₄ particle showed slightly decay of oxidation reactivity as the number of cycle increased and oxidation rates (slope of breakthrough curve) were slower than other particles. These results indicate that the CoₓOᵧ/CoAl₂O₄ particle can cause some problems during long-term operation.

![Graph showing O₂ concentration profiles](image)

Fig. 5. O₂ concentration profiles during successive oxidation cycles.

**Conclusion**

Cyclic reduction and oxidation characteristics of four oxygen carrier particles by using syngas as fuel have been investigated. Four particles, NiO/bentonite, NiO/NiAl₂O₄, CoₓOᵧ/CoAl₂O₄, OCN-650 were used as oxygen carrier particles. Simulated syngas and air
were used as reactants for reduction and oxidation, respectively. To check feasibility of good performance, inherent CO\textsubscript{2} separation, and low-NO\textsubscript{x} emissions, CH\textsubscript{4}, CO, CO\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}, NO, NO\textsubscript{x}, N\textsubscript{2}O concentrations were measured by on-line gas analyzer. Moreover, the regeneration ability of the oxygen carrier particles was investigated by successive reduction–oxidation cyclic tests up to the 10\textsuperscript{th} cycle. All four oxygen carrier particles showed high gas conversion, high CO\textsubscript{2} selectivity, and low CO concentration during reduction and no NO\textsubscript{x} (NO, NO\textsubscript{2}, N\textsubscript{2}O) emissions during oxidation. Moreover, all four particles showed good regeneration ability during successive reduction-oxidation cyclic tests up to the 10\textsuperscript{th} cycle. These results indicate that inherent CO\textsubscript{2} separation, NO\textsubscript{x}-free combustion, and long-term operation without reactivity decay of oxygen carrier particles are possible in the syngas fueled chemical-looping combustion system with NiO/beetonite, Ni/NiAl\textsubscript{2}O\textsubscript{4}, Co\textsubscript{x}O\textsubscript{y}/CoAl\textsubscript{2}O\textsubscript{4} and OCN-650 particles. However, Co\textsubscript{x}O\textsubscript{y}/CoAl\textsubscript{2}O\textsubscript{4} represented slightly decay of oxidation reactivity with the number of cycles increased and the oxidation rate is slower than other particles.

Acknowledgement

This work was supported by Ministry of Knowledge Economy (MKE) through Electric Power Industry Technology Evaluation & Planning Center (ETEP).

References