Synthesis and Redox Properties of NiO/\(\text{NiAl}_2\text{O}_4\) Oxygen Carriers for Hydrogen-Fueled Chemical-Looping Combustion

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Abstract: Hydrogen-fueled chemical-looping combustion (H-CLC), involving the reduction of a metal oxide with hydrogen and the oxidation of the reduced metal with oxygen in air, is a new combustion system that has been recently proposed to save energy and to suppress environmental impact. \(\text{NiO/\text{NiAl}_2\text{O}_4}\)-based oxygen carriers for H-CLC were prepared using a combination of sol-gel and oil-drop granulation methods, starting from precursors that are commonly used to prepare nickel oxide and alumina. The redox reactions of the oxygen carriers were carried out using a thermogravimetric reactor to identify the reactivity and regeneration properties. As a result, spherical particles with \(\sim 2\) mm diameters were prepared by the method applied in this study. X-Ray diffraction patterns indicated that the samples calcined at \(1573\) K were converted to a pure \(\alpha\)-alumina, a mixture of \(\alpha\)-alumina and \(\text{NiAl}_2\text{O}_4\), or a mixture of \(\text{NiAl}_2\text{O}_4\) and \(\text{NiO}\), depending upon nickel content in the starting materials. Our results indicate that an almost stoichiometric reaction between \(\text{NiO}\) and alumina occurs to form \(\text{NiAl}_2\text{O}_4\) during calcination. In the 10th cyclic tests of the reduction at \(873\) K with \(\text{H}_2\) and the oxidation at \(1273\) K with air, \(\text{NiO/\text{NiAl}_2\text{O}_4}\)-based carriers containing \(57 \sim 83\) wt\% \(\text{NiO}\) exhibit almost complete conversions, high redox reaction rates, and good regeneration properties. These results suggest that the combination of sol-gel and oil-drop granulation methods is a good approach toward increasing the quantity of active metal oxides in oxygen carriers for H-CLC.

Keywords: chemical-looping combustion, \(\text{NiO/\text{NiAl}_2\text{O}_4}\) oxygen carrier, spherical particle, hydrogen utilization

Introduction

Most energy-related industries are based essentially on the use of fossil fuels as their main energy source, but this dependence is accompanied by many problems, such as the exhaust of fossil fuel, air pollution, and global warming. Therefore, technologies for utilization of hydrogen fuel as an environmentally friendly and sustainable energy source are gaining attention worldwide. Some time ago, a hydrogen-fueled chemical-looping combustion (H-CLC) system for power plants was proposed by Jin and Ishida as a potential technology for hydrogen utilization [1,2]. In this combustion system, the active metal oxide component in an oxygen carrier is reduced by hydrogen (\(\text{H}_2 + \text{MO} \rightarrow \text{M} + \text{H}_2\text{O}\); \(\text{MO}\): metal oxide; \(\text{M}\): metal) at ca. \(600 \sim 900\) K in the reduction reactor and the reduced metal is reoxidized by oxygen in air (\(\text{M} + \frac{1}{2}\text{O}_2 \rightarrow \text{MO}\)) at ca. \(1200 \sim 1500\) K in a separated oxidation reactor. The solid oxygen carrier is repeatedly cycled in two interconnected reactors and the summation of two reactions is identical with the hydrogen oxidation of air. The exhaust gases from both reactors can be used as the working fluid to generate power in turbines. It was reported that the H-CLC system may provide the following advantages. The formation of \(\text{CO}_2\) and \(\text{NO}_x\) can be thoroughly excluded, because the fuel is only hydrogen and the oxidation reaction takes place without a flame. Higher efficiency power generation in the H-CLC system is possible, as compared with that of a gas turbine cycle with \(\text{H}_2/\text{O}_2\) combustion, because pure steam in the reduction reactor can be obtained without the use of pure oxygen [3-5].

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The key to the success of implementing an H-CLC system is the development of a good oxygen carrier, consisting of the active metal oxide component and the binder material. The oxygen carrier used in this combustion system should provide fast reduction and oxidation rates, higher oxygen carrier capacity, which corresponds to the amount of active metal oxide added, and higher mechanical stability for cyclic use. For this purpose, the selection of a suitable binder material is also very important to enhance the oxidation rate at high temperature (as an oxide ion conductor) and to increase the mechanical strength of the oxygen carrier particles. Therefore, since the introduction of the concept of H-CLC, most previous investigations have focused on the development of oxygen carriers with higher performance in terms of their chemical composition. It was found that a NiO/Al2O3 material, at a weight ratio of 3:2, provided superior performance among the various oxygen carriers prepared by mixing active metal oxides (Ni, Fe, or Co-based oxides) and binder materials [Al2O3, YSZ (yttria-stabilized zirconia), NiAl2O4, TiO2, or MgO] [2,6-10]. Most oxygen carriers have been prepared by complicated procedures involving mechanical mixing or coprecipitation. Recently, we found that it was possible to increase the quantity of the active metal oxide component in the oxygen carrier without causing big differences in the redox reactivity and regeneration properties by applying a new preparation method [11]. The method is related to the sol-gel process for the synthesis of the metal oxide and the oil-drop granulation method for the preparation of the large spherical particles. It is well known that metal oxides synthesized by the sol-gel process are mechanically strong and possess high attrition resistance; the oil drop granulation method is often used industrially for the preparation of large spherical particles having diameters between 100 μm and 5 mm [12-14]. It was reported by Wang and Lin [15] that a granulation process that combines the above sol-gel and the oil-drop methods could be used to prepare spherical alumina particles having excellent mechanical properties. In previous studies of H-CLC systems, however, the combination of sol-gel and oil-drop granulation methods has never been investigated, despite the large potential for preparing good oxygen carriers.

The aim of this investigation was to study the preparation of spherical NiO/Al2O3 materials that provide high redox reaction rates and good regeneration properties for H-CLC systems. NiO/Al2O3 materials with different NiO contents were prepared by using a combination of sol-gel and oil-drop granulation methods. The physical and redox properties of the prepared NiO/Al2O3 materials were also investigated to select suitable oxygen carriers for H-CLC.

**Experimental**

**Preparation of Oxygen Carriers**

Various NiO/Al2O3 oxygen carriers were prepared through the use of Ni(NO3)2·6H2O and Al[OCH(CH3)2]3 as Ni and Al precursors, respectively, according to the following procedure. First, one mole of Al[OCH(CH3)2]3 was slowly added into 1 L of distilled water and stirred well at 353 K. Then, the desired amount of Ni(NO3)2·6H2O in aqueous solution was added to the sol solution, and further stirred at the same temperature for 3 h to form a uniform sol solution. The solution was acidified to pH 3 with a small amount of 1 M HNO3; the solvent was subsequently evaporated at 343 K under fast rotation using a rotary evaporator until a viscous mass remained. The mass was then transferred to dropppers and used as the starting material for the granulation process. Sol droplets from the dropper were passed through a paraffin oil layer (density: 0.75 g/cm3; height of oil layer: ca. 20 cm), accompanied with shaping and partial gelation, and then entered into a 10 wt% ammonia solution layer, where the spherically shaped granules were further aged at room temperature for 3 h. The spherical wet-gel granules were carefully washed with a mixture of water and alcohol and then dried at room temperature for 3 h and, subsequently, at 373 K for 24 h. The resulting dry-gel granules were calcined in air at 773 K for 3 h and, subsequently, at 1573 K for 6 h to give the final spherical particles with 1–2 mm diameters.

**Characterization of Oxygen Carriers**

The surface areas of the prepared particles were
Table 1. Characteristic Data of the Prepared Materials

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Composition (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Sphericity</th>
<th>Crash strength (N/m²)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO</td>
<td>NA</td>
<td>AL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL-1</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>7.07</td>
<td>Very good</td>
</tr>
<tr>
<td>NAL-1</td>
<td>0</td>
<td>43</td>
<td>57</td>
<td>4.09</td>
<td>Very good</td>
</tr>
<tr>
<td>NAL-2</td>
<td>0</td>
<td>79</td>
<td>21</td>
<td>2.73</td>
<td>Very good</td>
</tr>
<tr>
<td>NiO-1</td>
<td>26</td>
<td>74</td>
<td>0</td>
<td>0.94</td>
<td>Very good</td>
</tr>
<tr>
<td>NiO-2</td>
<td>45</td>
<td>55</td>
<td>0</td>
<td>0.66</td>
<td>Good</td>
</tr>
<tr>
<td>NiO-3</td>
<td>57</td>
<td>43</td>
<td>0</td>
<td>0.50</td>
<td>Good</td>
</tr>
<tr>
<td>NiO-4</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>0.39</td>
<td>Good</td>
</tr>
<tr>
<td>NiO-5</td>
<td>83</td>
<td>17</td>
<td>0</td>
<td>0.31</td>
<td>Good</td>
</tr>
<tr>
<td>NiO-6</td>
<td>91</td>
<td>9</td>
<td>0</td>
<td>2.62</td>
<td>Fair</td>
</tr>
</tbody>
</table>

⁴ NA: NiAl₂O₄  
⁵ AL: α-Al₂O₃

Figure 2. X-Ray diffraction patterns of the prepared materials.

measured at 77 K by using a Micromeritics ASAP-2400 instrument, and the crystalline phases were characterized by the X-ray diffraction patterns obtained using a Rigaku Miniflex diffractometer and Cu Kα radiation. The surface morphologies of the oxygen carriers during the cyclic tests were also observed using a scanning electron microscope (SEM, Phillips XL-30). The crash strength was obtained from the minimum force required for one particle to be crashed, divided by the cross-sectional area of the particle.

Redox Reactivity Tests

Reductions and oxidations on the oxygen carriers were carried out in a reactor modified from a thermo-gravimetric analyzer (SETARAM TG-DTA-92), as shown in Figure 1. The sample (ca. 20 mg) was placed on an alumina pan and the temperature was increased at a rate of 20 K/min while purging with inert Ar gas. When a temperature of 873 K for reduction was reached, the reactant H₂ gas was passed through the reactor by substituting it for the Ar gas. After reduction of the sample for 20 min, the gas supplied to the reactor was changed to inert Ar gas and then the temperature was increased to 1273 K at a rate of 20 K/min. The reduced sample was reoxidized by the changed air gas at 1273 K for 20 min. Using the same procedure described above for reduction and oxidation, 10 cyclic tests were performed repeatedly to evaluate the durability of the sample. In all experiments, the weight change of the sample and the reaction temperature were recorded continuously by using a computer; the total flow rate of the gases supplied to the reactor was always fixed at 100 mL/min (at standard state).

Results and Discussion

Characterization of Prepared Materials

Table 1 provides the physical properties and compositions of the materials prepared in this study. Upon increasing the Ni content in the Ni and Al precursors, the chemical components in the prepared materials were first converted to a mixture of α-alumina and NiAl₂O₄ (NAL-1, NAL-2) and subsequently converted to a mixture of NiO and NiAl₂O₄ (NiO-1 ~ NiO-6), as evidenced from the X-ray diffraction patterns in Figure 2. In the case of the NiO/NiAl₂O₄ mixture, especially, the peaks for α-alumina in the X-ray diffraction patterns were almost observe, indicating that an almost stoichiometric reaction between NiO and alumina occurs to form NiAl₂O₄. Therefore, the composition of each component was calculated on the basis of the amounts of Ni and Al in the starting materials, and the calculated amounts of NiO in the NiO/NiAl₂O₄ mixtures were provided as the amount of active metal oxide that takes part in the redox reaction.

On the other hand, the BET surface areas for the micropores of the prepared materials were very low (below ca. 7 m²/g) because of the high calcination
temperature (1573 K) and the gradually decreased upon increasing the Ni content besides a NiO-6 oxygen carrier. The sphericity and crash strength of these materials were relatively superior on the whole, even though these properties deteriorated upon increasing the Ni content. In the case of the NiO-3 oxygen carrier with ca. 57 wt% NiO, especially, the crash strength (8.2 × 10^6 N/m²) was about two times higher than that of the NiO/NiAl₂O₄ oxygen carrier of similar composition (3.5 × 10^6 N/m²) reported by Jin and coworkers [8]. In addition, the colors of the prepared materials were blue for the mixture of α-alumina and NiAl₂O₄ (NAL-1, NAL-2) and green for the mixture of NiO and NiAl₂O₄.

**Figure 3.** Effect of the NiO content in the NiO/NiAl₂O₄ oxygen carriers on (A) the reduction by H₂ at 873 K and (B) the oxidation by air at 1273 K.

**Figure 4.** Effects of 10 cycles of reduction and oxidation on the regeneration properties of a NiO-5 oxygen carrier.

**Redox Reaction Kinetics of the NiO/NiAl₂O₄ Oxygen Carriers**

The NiO/NiAl₂O₄ oxygen carriers (NiO-2 ~ NiO-6) with considerable amounts of NiO as the active metal oxide component were chosen to observe the kinetic behavior of the redox reaction. The reductions and oxidations were conducted at 873 K with H₂ and at 1273 K with air, respectively.

The changes in the fractional oxidation X on the oxygen carriers are plotted with respect to the reaction time, as shown in Figure 3. X is defined as (W-Wₜ)/(W₀-Wₜ), where W, W₀, and Wₜ are the instantaneous weight, the completely reduced weight, and the completely oxidized weight (i.e., initial weight), respectively. In all NiO/NiAl₂O₄ oxygen carriers with NiO contents above 57 wt% (NiO-3 ~ NiO-6), we found that both of the reduction and oxidation proceeded much faster, the times required for almost complete conversion were below 600 s. In the case of NiO-2 with a low NiO content (45 wt%), however, a decrease in the reduction rate and a big decrease in the oxidation rate were observed. This result indicates that an upper limit for the NiAl₂O₄ binder content exists to provide high solid diffusivity for oxide ions, especially in the NiO/NiAl₂O₄ oxygen carriers prepared by the combination of sol-gel and oil-drop methods, unlike those prepared by Jin and coworkers [8].

**Regeneration Properties of the NiO/NiAl₂O₄ Oxygen Carriers**

Regeneration is one of the most important problems faced for the industrial application of H-CLC. The NiO/NiAl₂O₄ oxygen carriers having NiO contents between 57 ~ 83 wt% (NiO-3 ~ NiO-5) exhibited similar regeneration properties during 10 cycles of reduction with H₂ the oxidation with air. The weight change in the
cyclic test using a NiO-5 carrier, as a representative example of the above three oxygen carriers, was plotted with respect to the reaction time, as shown in Figure 4. The weight of the NiO-5 carrier decreased through rapid reduction of NiO to Ni. During the cyclic tests, the oxidation from Ni to NiO was also fast and the final weights of oxidation almost returned to the initial weight.

Figure 5 shows scanning electron micrographs that indicate the surface morphologies of the NiO-5 carrier during the course of a reaction. Comparing the fresh NiO-5 carrier and the NiO-5 carrier obtained after the 10th cycle, we observe that macropores (> 1 μm) developed between the grains, but the surface morphologies between both carriers did not change greatly. This result indicates that the pore structures of the NiO/NiAl2O4 carriers with NiO contents between 57 ~ 83 wt% were relatively stable during the course of the cyclic reaction.

In the 10-cycle tests of a NiO-6 carrier having a high NiO content (91 %), however, the weight of the reduced NiO-6 carrier increased slightly until the 6th cycle, indicating that some changes occurred to the microstructure of the NiO-6 carrier. After the 7th cycle, the weight of the oxidized NiO-6 carrier did not fully recover and it decreased drastically. Drastic changes in the surface morphology of the NiO-6 carrier were also observed between the 6th and 10th cycles from scanning electron micrographs, as shown in Figure 7. In Figure 7(B), especially, pores are rare, indicating that the aggregation of reduced metals was accompanied by collapse of the pores [11]. Therefore, the very low reaction rates were caused by a very small number of pores. We deduce from these results that the diffusion of the reactive gases for the H-CLC is influenced to a greater by the existence of macropores, than by micropores, in the oxygen carrier.

On the other hand, the results above comparing NiO-5 and NiO-6 demonstrate that the NiAl2O4 binder content strongly affected the mechanical strength of the oxygen carriers as the number of cycles increased. This result means that a lower limit of the NiAl2O4 binder content exists to give mechanical stability to the NiO/NiAl2O4 oxygen carriers, even though a minimization of binder content is desired to provide a high oxygen carrier capacity. Conclusively, NiO/NiAl2O4 oxygen carriers with higher oxygen carrier capacities (up to 83 wt% NiO) than those reported previously were prepared by a method advanced in this paper. This preparation method may also provide economical advantages for mass production, because a commercial alumina sol, such as boehmite sol, can be used [16] and because this method is much simpler than that reported by Jin and coworkers [8].

**Conclusion**

The synthesis of NiO/NiAl2O4 oxygen carriers and their redox properties within a thermogravimetric reactor were investigated to develop superior oxygen carriers for H-CLC.
The advanced preparation method, a combination of sol-gel and oil-drop granulation methods, is highly effective and provides spherical NiO/NiAl₂O₄ materials (between 1–2 mm diameters) of high strength and well-dispersed NiO. The X-ray diffraction patterns obtained at different composition ratios indicate that well-networked materials formed between the Ni and Al precursors and, subsequently, NiO/NiAl₂O₄ materials formed in situ during the calcination stage. In the first cycle of the redox reaction, NiO/NiAl₂O₄ materials with NiO contents above 57 wt% displayed high reaction rates and almost complete conversions. In the 10-cycle redox reactions, however, the NiO/NiAl₂O₄ material having a NiO content of 91 wt% underwent undesired degradation of the mechanical stability. NiO/NiAl₂O₄ oxygen carriers with high NiO contents (57–83 wt%), that exhibit high redox reaction rates and good regeneration properties, were prepared using the method advanced in this paper. Minimization of the NiAl₂O₄ binder content must be limited, however, to maintain the mechanical stability of the oxygen carriers.

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References