Effect of the Addition of CeO2 or MgO on the Oxygen Carrier Capacity and Rate of Redox Reactions of NiO/Fe2O3/Al2O3 Oxygen Carriers

Kyeongsook Kim†, Seugran Yang†, and Keesam Shin‡,*

†Creative Future Laboratory, Korea Electric Power Corporation (KEPCO) Research Institute, 105 Munji-Ro, Yuseong-gu, Daejeon 34056, Republic of Korea
‡School of Nano & Advanced Materials Engineering, Changwon National University, 20 Changwondaehak-ro, Uichang-gu, Changwon, Gyeongsangnam-do 51140, Republic of Korea

ABSTRACT: Two compositions of mixed oxygen carriers (OCs), N1F1A1 (mole ratio of NiO to Fe2O3 is 1:1) and N1F2 (mole ratio of NiO to Fe2O3 is 1:2), were fabricated by mechanical mixing, and the effects of CeO2 and MgO additives on the oxygen-transfer capacity (OTC) and crystal structure were analyzed. In addition, X-ray diffractionometry after the oxidation and the reduction steps was carried out to determine the reaction mechanism. Potential mixed OCs of the candidates of various OCs, such as NiO/Fe2O3, are proposed based on the OTC and oxygen-transfer rate evaluated via X-ray diffraction (XRD) phase analysis and thermogravimetric analysis. The chemical reaction equation for the oxidation and reduction was suggested based on the XRD characterization of the phases including NiFe2O4 and MgAl2O4 in N1F1A1 (①) and N1F1A1-Mg5 (④). Addition of MgO is confirmed to enhance the OTC and oxygen-transfer rate. The mechanism of the oxidation and reduction of metal oxides and the role of MgO were suggested. Even though the addition of MgO does not transfer oxygen to the fuel, it does accelerate the oxidation and reduction reactions of NiFe2O4.

1. INTRODUCTION

Chemical-looping combustion (CLC) technology, an indirect combustion technology using oxygen carriers (OCs), is seen as a possible system for low-cost CO2 capture with low power losses. CLC consists of an oxidation reactor (combustion of metals) and a reduction reactor (organic fuel combustion), between which the OC continuously circulates.1−3 CH4 and syngas are usually used as the organic fuel, and there are some reports on the usage of coal (Figure 1).4−8

Optimization of OC is the key to successful exploitation of CLC technology. The key characteristics to optimize are their oxygen-transfer capacity (OTC), oxygen-transfer rate, and properties for fluidization (shape, size, and compaction density) and high durability (strength and heat resistance) because they will be used for extended periods of time in a fluidized bed at 900−1100 °C. Metal oxides such as Mn2O3, Fe2O3, NiO, CuO, and CoO have been used as OCs on supports such as bentonite, yttria-stabilized zirconia, Al2O3, MgO, TiO2, NiAl2O4, MgAl2O4, SiO2, and ZrO2. Since 2008, NiO on an Al2O3 support has been viewed as the best OC for CLC.9−16

We are working on the scale-up of a system to 1−10 MW, based on the successful 100+ hour operation of a 200 kW gas circulation combustion system using NiO/Al2O3 OC produced by gas atomization.17 Nickel oxide is expensive, and nickel compounds are toxic. Thus, finding reasonable supplemental materials that cancel out any loss in the CLC profitability by their low cost is useful. It has been estimated that replacing about 30% of the NiO with iron oxides could lower costs substantially despite decreasing the reaction efficiency.18−20 These cost reductions become significant when considering the material requirements of a 300 MW plant over a single year—about 100 tons. Should solid organic fuels be used rather than syngas, costs are expected to sink even further.21,22

In addition to the basic MO-on-support structure described above, improvements to the CLC parameters have been gained as a result of the addition of other MO components. Examples include alkali metal oxides, Li2O and K2O. Ab initio DPF (density functional theory) was used to study the synergistic effects of MgO in interactions of CO, O2, and Fe2O3.23

Figure 1. CLC (M: metal, MO: metal oxide).
most interesting is CeO₂, which accelerates the catalytic activity or even modifies the characteristics of the transition metals (Fe, Co, and Ni). CeO₂ is reported to have a high oxygen storage capacity because of the high redox potential and strong interaction between support metals and Ce.²⁴–²⁷

In this paper, OC mixtures of NiO and Fe₂O₃ with molar ratios of 1:1 and 1:2 with added CeO₂ and MgO are investigated. The mechanical properties of all the fabricated CLC media tested here are the same so that differences in their chemical reactivities can be assessed. We propose a reaction mechanism for the oxidation and reduction steps based on phase analyses of the specimens at each step.

2. EXPERIMENTAL SECTION

2.1. Materials and Fabrication Method. The starting materials are NiO (nickel oxide green), Fe₂O₃ (iron oxide red 3150 RM Deqing United Pigment Co., Ltd.), γ-Al₂O₃ (vgl-15 Union Showa K.K.), and CeO₂ and MgO, all >98% purity. The OC was fabricated via mechanical mixing, dried for 24 h in a convection oven, and calcined in an air environment muffle furnace whose temperature was set to 1100 °C.

2.2. Measurements. The OTC and oxygen-transfer rate were measured by thermogravimetric analysis (TGA) (Linseis) in 10% methane and 90% CO₂ gas for reduction and in air for oxidation at 950 °C under the conditions listed in Table 1.

### Table 1. TGA Conditions

| item                | conditions          |
|---------------------|---------------------|
| sample weight       | 30 mg               |
| gas flow rate       | 300 s               |
| isothermal temperature | 950 °C             |
| inert gas injection time | 5 min              |
| reduction gas       | CH₄ (10 vol%) + CO₂ (90 vol%) |
| oxidation gas       | air (100 vol%)      |
| inert gas           | N₂ (100 vol%)       |
| oxidation time      | 10 min              |
| reduction time      | 10 min              |

Oxidation and reduction were repeated for at least five cycles with a 5 min nitrogen gas purge in between steps. The crystal structure was analyzed by X-ray diffraction (XRD; D/Max 2200 Rigaku International) at 40 kV, 30 mA of Cu Kα, in the range of 10–100° for 2θ. XRD patterns were taken after each oxidation and reduction step to elucidate the reaction mechanism.

2.3. Calculations. For the selection of the optimum candidates, OC particles are evaluated for the mechanical property such as wear resistance and reactivity. However, only the reactivity was assessed because the screening of the OCs of similar mechanical properties is the main purpose of this study. TGA gives a measurement of the OTC of the mixed OC, Cₜ, which is the highest oxygen-transfer ratio of the OC for given reaction conditions, as given in eq 1.

\[ Cₜ = (m_{ox} - m)/m_{ox} \]  

(1)

where \( m_{ox} \) is the mass of the particles upon complete oxidation of the OC particles and \( m \) is the mass of the particles upon complete reduction of the OC particles, as measured by TGA.

The Cₜ thus determined is compared to the theoretical value, \( R_{ox} \), derived from the stoichiometry of the MO. The oxygen-transfer rate is expressed as \( dx/dt \), where \( x \) is given by

\[ x = (m_{ox} - m)/(m_{ox} - m_{red}) \]  

(2)

where \( m_{red} \) is the mass of the particles upon complete reduction of the OC particles.

XRD patterns are taken to determine the effect of the crystal structure on the OTC and oxygen-transfer rate, as measured by TGA.

3. RESULTS AND DISCUSSION

The theoretical value \( R_{ox} \) of the OTC is calculated based on the stoichiometry of the MO. The high OTC for all eight specimens of this study is probably partly due to the method of fabrication, mechanical mixing, and the low calcination temperature of 1100 °C. Specimens fabricated via spray-drying tend to lower the OTC values than the theoretically predicted ones. This is because OTC decreases as the calcination temperature increases.

3.1. NiO/Fe₂O₃/Al₂O₃ Mixed Metal Oxide (N1F1A1).

#### 3.1.1. N1F1A1 Composition. In Table 2, the OC specimens are listed with the weight fraction of the oxides, where N1F1 indicates a 1:1 molar ratio in NiO and Fe₂O₃, C5 and C10, respectively, contain 5 and 10% CeO₂, and Mg5 contains 5% MgO.

### Table 2. Nomenclature and Composition of N1F1A1 (wt%)

| sample/compounds | NiO | Fe₂O₃ | Al₂O₃ | CeO₂ | MgO |
|------------------|-----|-------|-------|------|-----|
| N1F1A1           | 22.5| 47.5  | 30.0  | 5.0  | 5.0 |
| N1F1A1CS         | 21.0| 45.0  | 27.0  | 10.0 | 5.0 |
| N1F1A1C10        | 20.0| 43.0  | 27.0  | 10.0 | 5.0 |
| N1F1A1M5         | 21.0| 45.0  | 29.0  | 5.0  | 5.0 |

3.1.2. Oxygen-Transfer Capacity. Table 3 shows the OTC measured by TGA along with the theoretical values. When compared to N1F1A1 without additive, addition of MgO 5% improves the OTC more than CeO₂ 10% as shown by the highest measured OTC of 8.45 of the mixed metal oxide.

### Table 3. OTC of N1F1A1 (wt%), Averaged with Five Cycles in TGA

| mixed metal oxide/OTC | theoretical OTC | measured OTC |
|-----------------------|-----------------|--------------|
| N1F1A1                | 6.15            | 8.12         |
| N1F1A1CS              | 5.76            | 6.92         |
| N1F1A1C10             | 5.49            | 7.64         |
| N1F1A1M5              | 5.76            | 8.45         |

The mass-based conversion as a function of reaction time of reduction and oxidation is shown in Figure 2. As Figure 2 shows, the reduction of single metal oxide OCs, that is, N70 (NiO 70% + Al₂O₃ 30% as a support) and Fe70 (Fe₂O₃ 70% + Al₂O₃ 30% as a support), completed in a few minutes, whereas N1F1A1 (the mixed OC) took 7–9 min to complete the reduction. However, the oxidation reaction was completed in 2 min, regardless of the composition. The time needed to complete the reduction in increasing order is CeO₂ (7.8 min), NiO (8.2 min), Fe₂O₃ (8.4 min), and MgO (8.9 min).

3.1.3. Crystal Structure Analysis. Table 4 lists the major peak intensities of the XRD patterns. The specimens of CeO₂ and MgO 5% characteristically showed NiFe₂O₄, Al₂O₃, and residual CeO₂. On the other hand, specimen CeO₂ has MgAl₂O₄ and MgFeAlO₄ peaks in addition to the major peaks of NiFe₂O₄, Al₂O₃, and Fe₂O₃ (Figure 3).
This is attributed to the reaction of NiO and Fe$_2$O$_3$ resulting in NiFe$_2$O$_4$ with residual Al$_2$O$_3$ and CeO$_2$ in ①, ②, and ③. In ④, all NiO reacts with Fe$_2$O$_3$, forming NiFe$_2$O$_4$, whereas all MgO reacts with Al$_2$O$_3$ and Fe$_2$O$_3$, forming MgAl$_2$O$_4$ and MgFeAlO$_4$, leaving residual Al$_2$O$_3$ and Fe$_2$O$_3$.

The possible reaction equations involving NiO, Fe$_2$O$_3$, and Al$_2$O$_3$ are as follows:

\[
\begin{align*}
\text{NiO} + \text{Al}_2\text{O}_3 & \rightarrow \text{NiAl}_2\text{O}_4 \\
\text{Fe}_2\text{O}_3 + 2\text{Al}_2\text{O}_3 & \rightarrow 2\text{FeAl}_2\text{O}_4 \\
\text{NiO} + \text{Fe}_2\text{O}_3 & \rightarrow \text{NiFe}_2\text{O}_4 \\
2\text{NiO} + \text{Fe}_2\text{O}_3 + 3\text{Al}_2\text{O}_3 & \rightarrow 2\text{Ni}(\text{Al}, \text{Fe})_2\text{O}_5
\end{align*}
\]

The XRD patterns indicate that reaction 5 is the major working mechanism in the NiO/Fe$_2$O$_3$/Al$_2$O$_3$ mixed OCs because the XRD patterns do not show phases indicated by reactions 3, 4, and 6 (Figure 2). In ①, ②, and ③, the measured values of OTC are higher than the theoretical predicted values because of the formation of NiFe$_2$O$_4$; the presence of residual Al$_2$O$_3$ and CeO$_2$ indicates that CeO$_2$ does not influence the system significantly. On the other hand, the fact that MgAl$_2$O$_4$ and MgFeAlO$_4$ are formed in addition to NiFe$_2$O$_4$ in ④ is taken as an indication of the participation of MgO in the reaction, resulting in the improvement of OTC and oxygen-transfer rate.

NiFe$_2$O$_4$ was formed when the molar ratio of NiO, Fe$_2$O$_3$, and Al$_2$O$_3$ was 1:1:1 with added CeO$_2$ or MgO. These mixtures yielded higher OTC than that predicted by the theory, thanks to the high oxygen content of NiFe$_2$O$_4$ (24 wt%) compared to that of NiO (21 wt%). With the MgO addition (④), OTC and oxygen-transfer rate were the highest, which is attributed to the accelerated formation of NiFe$_2$O$_4$ and additional role of MgFeAlO$_4$ presumably.

Consequently, N1F1A1 OC was fabricated with a 1:1:1 molar ratio of NiO, Fe$_2$O$_3$, and Al$_2$O$_3$ with CeO$_2$ addition, and the potential binder species, NiAl$_2$O$_4$, was not formed. However, when MgO is added, the peaks of MgAl$_2$O$_4$ and MgFeAlO$_4$ are observed. The measured OTC values of 1.2−1.5 times the theoretical OTC value are considered to be due to the formation of NiFe$_2$O$_4$ (24 wt%), as shown by the highest intensity peak in the XRD pattern (Figure 3).

### 3.2. NiO/Fe$_2$O$_3$ Mixed Metal Oxide (N1F2)

#### 3.2.1. N1F2 Composition

Table 5 lists the compositions of the sample compounds; N1F2 designates the sample with a molar ratio 1:2 of NiO to Fe$_2$O$_3$, C5, C10, and M5 correspond to 5 and 10% of CeO$_2$ and 5% of MgO, respectively.

#### 3.2.2. Oxygen-Transfer Capacity

Table 6 shows that the OTCs of the specimens listed in Table 5 are comparable and about 2 times the theoretical values.

As shown in Figure 4, the mixed oxides of N1F2 composition took 6−10 min for reduction and less than 5 min for oxidation (on the right side of the graph). The order of the reduction rate of the specimens (duration until the completion of the reaction) is ⑧ (6.2 min), ⑦ (7.2 min), ⑤ (7.6 min), and ⑥ (10 min), and the order of the oxidation rate (duration until the completion of the reaction) is ⑤ (2.5 min), ⑧ (3.0 min), and ⑥, ⑦ (4.5 min). Thus, the sample with 5% MgO showed
the highest reaction rate, while the amount of CeO$_2$ content seems to have no effect on the reaction rates.

### 3.2.3. Crystal Structure Analysis.

Table 7 shows the major peaks and intensities of the XRD spectrum of the OCs in Table 5. N1F2 (⑤), N1F2C5 (⑥), and N1F2C10 (⑦) have peaks of NiFe$_2$O$_4$, Al$_2$O$_3$, and residual CeO$_2$, but N1F2M5 (⑧) has only NiFe$_2$O$_4$/MgFe$_2$O$_4$. In ⑤, ⑥, and ⑦, NiO and Fe$_2$O$_3$ reacted and yielded NiFe$_2$O$_4$ with residual Fe$_2$O$_3$ and CeO$_2$. However, N1F2M5 (⑧) behaves different from N1F1A1M5 (④) because of the presence of Al$_2$O$_3$. As shown in the XRD pattern of Figure 5, N1F2M5 (⑧) forms NiFe$_2$O$_4$ from the reaction of NiO and Fe$_2$O$_3$, and the residual Fe$_2$O$_3$ and MgO are believed to react to form MgFe$_3$O$_5$ and MgO from the reaction of MgFe$_3$O$_5$ and NiFe$_2$O$_4$. NiFe$_2$O$_4$ has a similar phase as shown by the angles and intensity of the XRD peaks (Figure 6).

### 3.3. Elucidation of Mechanism.

To elucidate the reaction mechanism and the effects of additives, XRD analyses were carried out for specimens obtained at the oxidation and reduction steps of N1F1A1 (①) and N1F1A1-M5 (④).

#### 3.3.1. N1F1A1 (①).

Figure 6 shows the XRD patterns of N1F1A1 (①), before TGA, after TGA oxidation, and after TGA reduction. The results indicate that NiFe$_2$O$_4$ is the main phase before and after the oxidation of (①), but NiFe$_2$O$_4$ disappears upon reduction and FeNi$_3$ and Fe$_2$O$_3$ form. Thus, we can confirm that N1F1A1 (①) forms NiFe$_2$O$_4$ through the reaction of NiO and Fe$_2$O$_3$ during calcination at 1100 °C. According to the results, it appears to remain as NiFe$_2$O$_4$ during oxidation and converts to FeNi$_3$ and Fe$_2$O$_3$ during reduction, as expressed in eq 7.

$$
6\text{NiFe}_2\text{O}_4 \rightleftharpoons 2\text{FeNi}_3 + 5\text{Fe}_2\text{O}_3 + 4.5\text{O}_2
$$

#### 3.3.2. N1F1A1-M5 (④).

The XRD patterns of N1F1A1M5 (④) before and after the oxidation and reduction (Figure 7) indicate that MgFeAl$_2$O$_4$ is the major phase upon oxidation, whereas MgAl$_2$O$_4$, MgO, and Fe$_2$O$_3$ are the major phases upon reduction. Equation 8 shows a possible reaction scheme, in which iron is displaced by Al from MgFeAl$_2$O$_4$ upon oxidation and reincorporated, yielding free oxygen, during reduction.

$$
2\text{MgFeAl}_2\text{O}_4 \rightleftharpoons \text{MgAl}_2\text{O}_4 + \text{MgO} + \text{Fe}_2\text{O}_3
$$
4. CONCLUSIONS

Eight OCs (four each of N1F1A1 and N1F2) were fabricated via mechanical mixing, and their OTC and crystal structure were analyzed to determine the effect of additives, CeO₂ and MgO. The reaction mechanism was found by analyzing the phases of N1F1A1 and N1F1A1M5.

(1) It is known that the OTC of OCs fabricated by spray-drying is lower than the predicted theoretical values and is lowered as the calcination temperature is increased. Our OTCs are higher because the samples are made by mechanical mixing, and they are calcined at a lower temperature, 1100 °C.

(2) The reduction and oxidation were completed within 7–9 min and 2 min, respectively. The OTCs were 1.2–1.5 times the theoretical value. This is attributed to the high fraction of NiFe₂O₄ (24 wt%), which has a higher OTC than NiO. In N1F1A1, NiAl₂O₄, which can act as a binder, was not formed. However, NiAl₂O₄ and MgFeAl₂O₄ peaks were observed when MgO was added.

(3) In N1F2, reduction and oxidation were completed within 6–10 min and within 5 min, respectively. The OTCs were measured as ~2 times the theoretical value because of the high fraction of NiFe₂O₄ (24 wt%), which has higher OTC than NiO.

(4) In N1F1A1, NiFe₂O₄ forms during calcination through the reaction of NiO, Fe₂O₃, and Al₂O₃, which converts to FeNi₃ and γ-alumina-supporting oxides: A comparative study. J. Solid State Chem. 1998, 135, 59–69.

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Addition of MgO is confirmed to enhance the OTC and oxygen-transfer rate. Even though the addition of MgO does not transfer oxygen to the fuel, it does accelerate the oxidation and reduction reactions of NiFe₂O₄.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: keesam@changwon.ac.kr. Phone: 82-55-213-3696.

ORCID
Keesam Shin: 0000-0002-9507-2087

Notes

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