Development of promotors for fast redox reaction of MgMnO$_3$ oxygen carrier material in chemical looping combustion

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MgO or gadolinium-doped ceria (GDC, Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$) was added as a promoter to improve the oxygen transfer kinetics of MgMnO$_3$ oxygen carrier material for chemical looping combustion. Neither MgO nor GDC reacted with MgMnO$_3$, even at the high temperature of 1100 $^\circ$C. The average oxygen transfer capacities of MgMnO$_3$, 5 wt% MgO-MgMnO$_3$, and 5 wt% GDC-MgMnO$_3$ were 8.74, 8.35, and 8.13 wt%, respectively. Although the addition of MgO or GDC decreased the oxygen transfer capacity, no further degradation was observed during their use in 5 redox cycles. The addition of GDC significantly improved the conversion rate for the reduction reaction of MgMnO$_3$ compared to the use of MgO due to an increase in the surface adsorption process of CH$_4$ via oxygen vacancies formed on the surface of GDC. On the other hand, the conversion rates for the oxidation reaction followed the order 5 wt% GDC-MgMnO$_3$ > 5 wt% MgO-MgMnO$_3$ > MgMnO$_3$ due to morphological change. MgO or GDC particles suppressed the grain growth of the reduced MgMnO$_3$ (i.e., (Mg,Mn)O) and increased the specific surface area, thereby increasing the number of active reaction sites.

Key words: Chemical looping combustion, Oxygen carrier material, Oxygen transfer capacity, Conversion rate, Promoter.

Introduction

As the global population grows, the amount of energy used increases year by year, and fossil fuel usage is far greater than that of other energy sources. Continued use of fossil fuels has increased emissions of carbon dioxide, which is accelerating global warming. Since the signing of the Paris Agreement on climate change, which defines a framework for responding to climate change, many countries around the world have attempted to shift their energy policy to reduce greenhouse gas usage [1]. Climate change policies are increasing interest in carbon dioxide capture and utilization technologies to reduce carbon dioxide emissions.

In recent years, a great deal of research has been conducted on chemical looping combustion (CLC) as a highly efficient technology for carbon dioxide capture. CLC technology has the advantage of flexible fuel use, being suited for the use of various organic fuels including coal, biomass, and natural gas [2-6]. A CLC system has a fuel reactor and an air reactor connected to each other, and oxygen carrier materials circulate between the reactors. In the fuel reactor, oxygen carrier materials in the oxidized state react with the fuel, becoming reduced and ultimately generating water and carbon dioxide. In the air reactor, the reduced oxygen carrier materials react with oxygen in the air to be oxidized, eventually generating unreacted oxygen and nitrogen. Between the fuel reactor and the air reactor, there is a loop seal chamber filled with oxygen carrier materials, so that the gases in the fuel and air reactors do not mix [7]. Therefore, high concentration of water and carbon dioxide can be obtained in the fuel reactor, and finally water can be condensed to obtain carbon dioxide. Because combustion in the fuel reactor takes place without flame, no thermal NOx is generated.

The oxygen carrier material used is very important in determining the efficiency of a CLC system because it transfers both oxygen and heat between the reactors. Oxygen carrier materials are normally oxides of Ni, Co, Cu, Mn, and Fe. Sometimes supports that are inert to the redox reaction can be used to prevent agglomeration, such as $\alpha$-Al$_2$O$_3$, $\gamma$-Al$_2$O$_3$, MgAl$_2$O$_4$, MgO, and CaO [8]. Ni- and Co-based oxides are known to have good oxygen transfer capability, but they are toxic and very expensive [9]. Although Fe-based oxides are inexpensive, their use results in slow redox reactions that produce many intermediate compounds [10, 11]. Cu-based oxides are also less expensive than Ni- and Co-based oxides, but have low melting points that limit their use in high-temperature reactors above 1000 $^\circ$C [12]. Contrastingly, Mn-based oxides are inexpensive, show stability at high temperature, and have relatively high reactivity. We recently developed a MgMnO$_3$ material having a defect cubic spinel crystal structure as a novel oxygen...
carrier material [13]. Although MgMnO₃ exhibits better oxygen transfer capacity retention during long-term cycling and a higher conversion rate than the well-known Mn-based oxide CaMn₀.₉Mg₀.₁O₃, it still shows slower redox reaction kinetics than the conventional oxygen carrier material NiO. The addition of CeO₂ or MgO can improve the oxygen carrier capacities and redox reaction rates of NiO/Fe₂O₃/Al₂O₃ oxygen carriers [14]. Moreover, because gadolinium-doped ceria (GDC, Ce₀.₉Gd₀.₁O₂₋δ) has an oxygen storage capability due to the formation of oxygen vacancies, this material can be expected to improve oxygen transport ability in reducing atmospheres [15, 16]. Accordingly, in the present work, MgO and GDC were separately tested as promoter additives to MgMnO₃. Herein, we describe the results of a systematic investigation of the oxygen transfer properties and redox kinetics of the resulting MgO- and GDC-MgMnO₃ composite oxygen carrier materials for CLC.

**Experimental Procedure**

MgMnO₃ powder was prepared by conventional solid-state reaction using Mn₂O₃ (CAS 1317-34-6; Alfa Aesar, UK) and MgO (CAS 1309-48-4; Alfa Aesar, UK) as precursors. Stoichiometric amounts of Mn₂O₃ and MgO were ball-milled with a zirconia ball in ethanol for 24 h at critical rotational speed. After ball-milling, they were dried at 100 °C in an oven for 1 d and then calcined at 1000 °C for 3 h. The calcined MgMnO₃ powder was mixed with 5 wt% of MgO or GDC (Kceracell Co. Ltd, Korea) powder by ball-milling with zirconia balls for 24 h in ethanol.

Phase analysis was carried out using X-ray diffraction (XRD; D/MAX-111A, Rigaku, Japan) with Cu Kα radiation. Diffraction patterns were recorded at a scan rate of 4°/min in the 2θ range of 20-80°. Microstructural changes were observed using field emission scanning electron microscopy (FE-SEM; SN-300, Hitachi, Japan).

Because the CLC process comprises oxidation reaction in an air reactor and reduction reaction in a fuel reactor, experimental equipment to evaluate the performance of oxygen carrier materials is needed to simulate the redox reaction. In this study, the oxygen transfer property of the oxygen carrier materials based on the redox reaction in the CLC process was evaluated by a thermal gravimetric analysis (TGA; TGA-N1000, Shinko, Korea) at 900 °C using 15% CH₄/CO₂ as the reducing gas and air as the oxidizing gas.

In each TGA experiment, a sample of 30 mg was loaded into an alumina basket. In redox cycle experiments, reducing gas and oxidizing gas were alternately flowed, each at the rate of 150 ml/min and for the duration of 10 min, with intervening 3 min periods of N₂ purging to prevent mixing of the reducing and oxidizing gases.

**Results and Discussion**

XRD patterns were collected of physical mixtures of MgMnO₃ with MgO or GDC powder (1 : 1 w/w) fired at 1100 °C for 3 h in air to determine whether MgMnO₃ reacted with the promoters and are shown in Fig. 1. The reflection peaks of the calcined mixed powders matched the ICDD patterns of MgMnO₃ (JCPDS#24-07360), MgO (JCPDS#45-0946), and GDC (JCPDS#75-0161), with no traces of secondary peaks. This indicates that the MgMnO₃ powders were chemically inert and stable and included the MgO or GDC promoter in an oxidized condition. Therefore, there is no problem using MgO- or GDC-MgMnO₃ composite as oxygen transfer materials at the operation temperature of 900 °C without changing the phase.

It has been reported that MgMnO₃ reacts with CH₄ and is reduced to MgO and MnO, thereby forming a
complete solid solution of \((\text{Mg,Mn})\text{O}\) with a 1 : 1 \(\text{Mg}/\text{Mn}\) ratio, namely \(\text{Mg_0.5Mn_0.5O}\) [13]. In XRD patterns of \(\text{MgO}\) or \(\text{GDC-MgMnO_3}\) composite samples reacted with \(\text{CH}_4\) for 1 h, the reflection peaks of the reduced powders were all matched with those in the patterns of \((\text{Mg,Mn})\text{O}, \text{MgO}, \text{and GDC}\) (Fig. 2), indicating that the \(\text{MgMnO_3}\) powders were also chemically inert and stable, with the \(\text{MgO}\) or \(\text{GDC}\) promoter in a reduced condition. Moreover, the molar ratio of \(\text{Mg}\) and \(\text{Mn}\) in a complete solid solution of \((\text{Mg,Mn})\text{O}\) can be determined using Vegard’s law. The lattice constant of 0.4358 nm was calculated for \((\text{Mg,Mn})\text{O}\) based on the XRD data shown in Fig. 2. The theoretical lattice constants of cubic \(\text{MgO}\) and \(\text{MnO}\) are 0.4218 and 0.4445 nm, respectively. The \(\text{MgO}\) content in the \((\text{Mg,Mn})\text{O}\) as calculated using Vegard’s law was 50.3%. This indicates that \(\text{Mn}\) in the \(\text{MgMnO}_3\) did not dissolve into the \(\text{MgO}\) promoter during the reduction reaction.

Based on the phase analysis, the redox reaction mechanism of the \(\text{MgO}\) or \(\text{GDC-MgMnO_3}\) composite can be described as follows:

\[
\begin{align*}
2\text{MgMnO}_3 + \text{CH}_4 + \chi(\text{MgO or GDC}) &\rightarrow 2(\text{Mg,Mn})\text{O} + \text{CO}_2 + 2\text{H}_2\text{O} + \chi(\text{MgO or GDC}) \quad (1) \\
2(\text{Mg,Mn})\text{O} + 2\text{O}_2 + \chi(\text{MgO or GDC}) &\rightarrow 2\text{MgMnO}_3 + \chi(\text{MgO or GDC}) \quad (2) \\
\text{CH}_4 + 2\text{O}_2 &\rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (3)
\end{align*}
\]

Because the overall reaction expressed by equation (3) is exothermic, the heat generated can be used to operate a steam turbine to produce electric power. On the other hand, methan e may react with transition metals to produce carbon [17, 18]. When carbon is deposited onto the oxygen carrier material in the fuel reactor, it can enter the air reactor with the oxygen carrier material, thereby undesirably generating carbon dioxide in the air reactor. Therefore, steam or carbon dioxide was injected with the oxygen carrier material to prevent carbon deposition due to the carbon–steam reaction \((\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2)\) and carbon dioxide reduction reaction \((\text{C} + \text{CO}_2 \rightarrow 2\text{CO})\), respectively [19, 20]. However, because these reactions are endothermic, they result in heat loss in the fuel reactor, thereby reducing the efficiency. Therefore, it is necessary to develop oxygen carrier materials that are tolerant to carbon deposition. Carbon deposition did not appear to occur in the present study; no carbon peak was observed in the Fig. 2 results even though the oxygen carrier materials were reduced using 100% \(\text{CH}_4\).

The conversion of oxygen carrier material during an oxidation or reduction reaction can be described by the change of weight \((m/m_{\text{ox}} \text{ or } m/m_{\text{red}})\) during TGA, which can be calculated from TGA data by dividing the mass at a specific time \((m)\) by the mass of the completely oxidized sample \((m_{\text{ox}})\) or the mass of the completely reduced sample \((m_{\text{red}})\). Therefore, the conversion ratios for reduction \((X_{\text{red}})\) and oxidation \((X_{\text{ox}})\) can be respectively calculated as \((m_{\text{ox}}-m)/m_{\text{ox}}\) and \((m-m_{\text{red}})/(m_{\text{ox}}-m_{\text{red}})\). The oxygen transfer capacity (OTC), which indicates how much oxygen can be delivered by the oxygen carrier material to react with fuel, can be calculated as \((m_{\text{ox}}-m_{\text{red}})/m_{\text{ox}}\).

During TGA at 900 °C, redox curves were collected during five redox cycles using \(\text{MgMnO}_3\), \(\text{MgO-MgMnO_3}\) composite, and \(\text{GDC-MgMnO_3}\) composite oxygen carrier materials; The amount of weight loss decreased slightly when \(\text{MgO}\) or \(\text{GDC}\) was included instead of using \(\text{MgMnO}_3\) alone (Fig. 3). This is because the \(\text{MgO}\) and \(\text{GDC}\) promoters play no role in the oxygen transfer. Table 1 lists the OTC values calculated from the data plotted in Fig. 3. The average OTCs of \(\text{MgMnO}_3\), \(\text{MgO-MgMnO_3}\) composite, and \(\text{GDC-MgMnO_3}\) composite oxygen carrier materials were 8.74, 8.35, and 8.13 wt%, respectively. The empirical OTC of \(\text{MgO-MgMnO_3}\) composite was similar to the

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**Table 1. Oxygen transfer capacities of \(\text{MgMnO}_3\), \(\text{MgO-MgMnO_3}\) composite, and \(\text{GDC-MgMnO_3}\) composite oxygen carrier materials during 5 redox cycles.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st cycle</th>
<th>2nd cycle</th>
<th>3rd cycle</th>
<th>4th cycle</th>
<th>5th cycle</th>
<th>Average</th>
</tr>
</thead>
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<tr>
<td>(\text{MgMnO}_3)</td>
<td>8.71</td>
<td>8.71</td>
<td>8.74</td>
<td>8.76</td>
<td>8.77</td>
<td>8.74</td>
</tr>
<tr>
<td>5 wt% (\text{MgO-MgMnO}_3)</td>
<td>8.24</td>
<td>8.34</td>
<td>8.38</td>
<td>8.39</td>
<td>8.42</td>
<td>8.35</td>
</tr>
<tr>
<td>5 wt% (\text{GDC-MgMnO}_3)</td>
<td>8.17</td>
<td>8.13</td>
<td>8.13</td>
<td>8.12</td>
<td>8.12</td>
<td>8.13</td>
</tr>
</tbody>
</table>

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**Fig. 3. Redox cycle curves of \(\text{MgMnO}_3\), \(\text{MgO-MgMnO_3}\) composite, and \(\text{GDC-MgMnO_3}\) composite oxygen carrier materials at 900 °C.**
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theoretical value of 8.30 wt% based on equation (1). Contrastingly, when GDC was added, the empirical OTC of GDC-MgMnO3 composite was 8.13%, slightly lower than the theoretical value of 8.30 wt%. This might have been due to the oxygen storage capability of GDC. It is well known that GDC can store oxygen due to oxygen vacancies and has been widely used as a catalyst [21]. Some of the oxygen from MgMnO3 might be stored in the GDC rather than reacting with CH4. This may account for the lower empirical OTC of the GDC-MgMnO3 composite compared to the calculated value. Meanwhile, no degradation of OTC was observed during the redox cycles, as shown in Fig. 3 and listed in Table 1. This indicates that neither MgO nor GDC adversely affected the oxygen transfer properties of MgMnO3 during the redox cycle.

The reaction rate dX/dt [%/s], representing the change in conversion rate per unit time, can be calculated from TGA data. Fig. 4 shows the reaction rates of the MgMnO3, MgO-MgMnO3 composite, and GDC-MgMnO3 composite oxygen carrier materials for the redox reaction versus the conversion ratios. Table 2 lists the maximum conversion rates during each cycle. The addition of MgO increased the conversion rate of the reduction reaction at conversion ratios of 0.4 or less. This indicates that MgO increased the initial reduction rate. Contrastingly, the conversion rate for the reduction was increased significantly throughout the reaction process by adding GDC, meaning that GDC is more effective than MgO. Unlike the catalytically inactive MgO, GDC can act as a catalyst. It is well known that the surface adsorption
reaction of the reaction gas is improved with increasing amounts of oxygen vacancies on the surface. Therefore, the significant improvement observed in the conversion rate of the GDC-MgMnO composite during the reduction reaction was due to an increase in the surface adsorption reaction of CH₄, which is a reaction gas, via the oxygen vacancies formed on the surface of GDC. Moreover, as shown in Figs. 5(g), (h), and (i), the well-dispersed fine GDC particles on the surface of MgMnO can extend the active sites for the solid-to-gas phase reaction.

Whereas the OTC showed no degradation during the redox cycle, as shown in Fig. 3 and Table 1, the maximum conversion rate for the reduction reaction tended to decrease with increasing number of redox cycles, as shown in Table 2. The maximum conversion rate of MgMnO₃ for the reduction reaction decreased significantly from the 1st to the 2nd cycle. Generally, the reaction rate decreases during continued redox cycling owing to microstructural change. As shown in Figs. 5(a) and (c), agglomeration was observed before and after the redox cycle, which we attribute to a significant reduction of the conversion rate of MgMnO₃. On the other hand, as shown in Figs. 5(d), (e), (f), (g), (h), and (i), the well-dispersed MgO or GDC particles in the MgO- or GDC-MgMnO composite oxygen carrier material suppressed the aggregation of MgMnO₃ particles and maintained the high reaction rate.

Regarding the conversion rate of the oxidation reaction, both the MgO- and GDC-MgMnO₃ composites exhibited much higher conversion rates than MgMnO₃. The maximum conversion rate for the 5th cycle of the oxidation reaction followed the order GDC-MgMnO₃ > MgO-MgMnO₃ > MgMnO₃. This trend can be explained with reference to the microstructure. When MgMnO₃ was reduced in 15% CH₄/CO₂, reduced MgMnO₃ was formed; namely, this was the porous material (Mg,Mn)O, which had much smaller grains compared with the initial MgMnO₃ owing to loss of oxygen and recombination of cations (Fig. 5(b)). The grain size of (Mg,Mn)O was decreased significantly by adding MgO or GDC due to their suppression of grain growth, as shown in Figs. 5(e) and (h). The GDC-MgMnO₃ composite had smaller grain size than the MgO-MgMnO₃ composite. As a result, the specific surface area per unit volume of the GDC-MgMnO₃ composite was larger than that of the MgO-MgMnO₃ composite. Because the conversion rate in the oxidation reaction increases in proportion to the number of active sites where oxygen can react, the maximum conversion rate for the oxidation reaction followed the order GDC-MgMnO₃ > MgO-MgMnO₃ > MgMnO₃.

Conclusions

MgO and GDC have been developed as promoters of the redox reaction of MgMnO₃ oxygen carrier material in chemical looping combustion. Both MgO and GDC showed compatibility with MgMnO₃ under both oxidation and reduction conditions at high temperature. Although the addition of MgO or GDC decreased the OTC, the conversion rate for the redox reaction increased significantly. Whereas MgO acted as an inactive material suppressing the agglomeration of MgMnO₃ particles, GDC not only inhibited agglomeration, but also catalytically promoted the reduction reaction; the surface adsorption reaction of the reaction gas was improved significantly due to the large number of oxygen vacancies on the GDC surface. In the oxidation reaction, the addition of MgO or GDC inhibited grain growth to provide much larger specific surface area than the initial MgMnO₃ without promoter, leading to a significant increase in the number of active sites for the oxidation reaction. Moreover, use of the MgO- or GDC-MgMnO₃ composite oxygen carrier materials maintained the OTCs and reaction rates during repeated redox cycling. Based on the above results, it can be concluded that GDC is superior to MgO as a promoter additive to MgMnO₃ oxygen carrier material for chemical looping combustion.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017R1D1A1B03031541). This work was also supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20184030202210).

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