

Effect of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ as a promoter upon the oxygen transfer properties of $\text{MgMnO}_{3-\delta}$ - $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ composite oxygen carrier materials for chemical looping combustion

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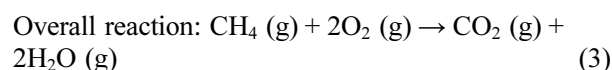
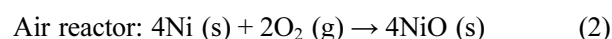
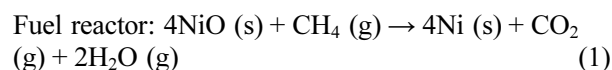
Chemical looping combustion (CLC) is a promising carbon capture and storage (CCS) technology whose efficiency and cost primarily relies on the oxygen carrier materials used. In this paper, gadolinium-doped ceria (GDC, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) was added as a promoter to improve the oxygen transfer rate of $\text{MgMnO}_{3-\delta}$ oxygen carrier materials. Increasing GDC content significantly increased the oxygen transfer rate of $\text{MgMnO}_{3-\delta}$ -GDC composites for the reduction reaction due to an increase in the surface adsorption of CH_4 via oxygen vacancies formed on the surface of the GDC. On the other hand, the oxygen transfer rate for the oxidation reaction decreased linearly with increasing GDC content due to the oxygen storage ability of GDC. Adsorbed oxygen molecules preferentially insert themselves into oxygen vacancies of the GDC lattice rather than reacting with (Mg,Mn)O to form $\text{MgMnO}_{3-\delta}$ during the oxidation reaction.

Key words: Chemical looping combustion, Oxygen carrier material, Re-dox reaction, Oxygen transfer capacity, Oxygen transfer rate.

Introduction

The primary energy supplied from natural resources is steadily increasing with global economic growth. With the rapid growth of the economy in recent years, traditional fossil fuels such as coal, oil, and LNG are projected to remain the main energy sources used in 2040, as reported by BP in their Statistical Review of World Energy [1]. Only a few years ago, it was predicted that the supply of renewable energy would increase smoothly in the era of high oil prices. However, with the recent development of shale gas, increases in fossil fuel prices have slowed and new renewable energy has become difficult to supply [2]. In addition, many developing countries tend to rely on cheap fossil fuels rather than expensive renewable energy sources [3]. The use of fossil fuels increases carbon dioxide emissions and is a major contributor to the greenhouse gases that are accelerating global warming [4]. Therefore, to address the inevitable increase in the use of fossil fuels, economical and highly efficient carbon capture and storage (CCS) technologies have been developed to capture CO_2 emitted from fossil fuels. CCS technologies are typically classified as pre-combustion, post-combustion, or oxy-fuel combustion technologies [5]. Chemical looping combustion (CLC)

technology, an oxy-fuel type, is attracting attention as a promising third-generation future energy technology [6]. CLC technology does not require CO_2 sequestration facilities because the CO_2 can be captured as part of the process [7]. Thus, CLC technology is more efficient than other CCS technologies. Also, the formation of NO_x gases is suppressed because CLC technology does not generate flame during the power generation, and the emissions of NO_x are accordingly less than those of other power generation technologies [8]. CLC technology uses two main reactors, interconnected with each other: an air reactor and a fuel reactor. Transition metal oxide is usually used as an oxygen carrier material. When CH_4 and NiO are respectively used as the fuel and the oxygen carrier material, the redox reactions are as follows.



Only water and CO_2 are exhausted from the fuel reactor, and if the water is condensed, pure CO_2 can be obtained. In the air reactor, unreacted air is discharged, so no pollutants are emitted. In the CLC process, the oxygen carrier material plays an important role not

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only in transferring heat between the reactors but also in transferring the oxygen required for combustion. Therefore, it is very important to develop high-performance oxygen carrier materials with high oxygen transfer rates, high oxygen transfer capacities, and excellent durability during the re-dox reaction. Crucially, because CLC involves operating temperatures between 900 and 1000 °C, metal particles in the oxygen carrier materials can easily become agglomerated during the reduction process, decreasing the specific surface area and thereby reducing reactivity with the fuel [9].

Oxides of Fe, Mn, Cu, Co, and Ni have been used as oxygen carrier materials in CLC [10, 11]. Although Co- and Ni-based oxides are state-of-the-art oxygen carrier materials due to their high reaction rates and high oxygen transfer capacities, they are very expensive. Recently, Mn-based oxides such as $MnFe_2O_4$, $CaMnO_3$, and $CuMn_2O_4$ have been investigated intensively; these are inexpensive, are stable under high temperatures, and show relatively high reactivity [12-14]. We have developed $MgMnO_{3-\delta}$ with cubic defect spinel structure as a highly efficient, low-cost, and stable oxygen carrier material, and reported its oxygen transfer capacity under 15% CH_4/CO_2 at 900 °C to be 8.74 wt% [15]. $MgMnO_{3-\delta}$ exhibited oxygen carrying stability during long-term cycling based on the result of the reversible re-dox reaction between $(Mg,Mn)O$ and $MgMnO_{3-\delta}$. However, although $MgMnO_{3-\delta}$ shows better oxygen transfer capacity retention and faster oxygen transfer rate than the well-known $CaMn_{0.9}Mg_{0.1}O_3$, it still has slow redox reaction kinetics compared to conventional oxygen carrier materials such as NiO.

To improve the properties of $MgMnO_{3-\delta}$, in the present work we added gadolinium-doped ceria (GDC, $Ce_{0.9}Gd_{0.1}O_{1.95}$), which has oxygen storage capability owing to its formation of oxygen vacancies, as a promoter to improve the oxygen transfer rate of $MgMnO_{3-\delta}$. The present report describes our systematic investigation of the effects of $Ce_{0.9}Gd_{0.1}O_{1.95}$ as a promoter upon the oxygen transfer properties of $MgMnO_{3-\delta}$ - $Ce_{0.9}Gd_{0.1}O_{1.95}$ composite oxygen carrier materials for CLC.

Experimental Procedure

$MgMnO_{3-\delta}$ powder was synthesized by means of a solid-state reaction method. Stoichiometric amounts of Mn_2O_3 (Alfa Aesar, UK) and MgO (Alfa Aesar, UK) were mixed by means of ball milling for 24 hrs followed by calcination in air at 1000 °C for 3 hrs. To make various formulations of composite oxygen carrier materials, the calcined $MgMnO_{3-\delta}$ powder was mixed with powder of a commercial GDC (Kceracell Co. Ltd., Korea) by means of ball milling with zirconia balls for 24 hrs in ethanol, and the resulting mixtures were sintered at 1200 °C for 3 hrs.

Phase analysis was carried out by means of X-ray diffraction analysis (XRD; D/MAX-111A, Rigaku,

Japan) using a Cu K α radiation source. Diffraction patterns were recorded at the scan rate of 4 °/min in the 2θ range of 20 ° to 80 °.

The oxygen transfer properties of $MgMnO_{3-\delta}$ -GDC composite oxygen carrier materials based on the re-dox reaction in the CLC process were evaluated by means of thermal gravimetric analysis (TGA; TGA-N1000, Shinko, Korea) at 900 °C. The amount of sample loaded for each TGA experiment was 30 mg. In the CLC system using CH_4 as the reaction gas in the fuel reactor, the product gases are H_2O and CO_2 , as shown in equation (1). Thus, the oxygen carrier materials are exposed to a CO_2 -rich atmosphere in the fuel reactor. Accordingly, 15% CH_4/CO_2 and air were used as the reducing and oxidizing gases, respectively; these were injected alternately into the fuel reactor during each re-dox cycle experiment. Between each reduction and oxidation step, the reactor was purged with N_2 for 3 min to prevent mixing of the reducing and oxidizing gases. The flow rate of each gas was 150 ml/min. Reduction and oxidation were carried out until the mass change rate was measured to be zero, which was assumed to indicate a complete reaction.

Temperature-programmed oxidation was also carried out using a TGA instrument to analyze the variation in the oxygen storage capability of GDC with temperature. The temperature was raised from room temperature to 900 °C at the heating rate of 3 °C/min.

Results and Discussion

The chemical stability of $MgMnO_{3-\delta}$ -GDC composites was investigated by means of XRD. XRD patterns of the physical mixture of $MgMnO_{3-\delta}$ with GDC powders fired in air at 1200 and 1300 °C for 3 hrs are shown in Fig. 1. All XRD peaks of the samples tested were matched with those of $MgMnO_3$ (JCPDS#24-07360) or GDC (JCPDS#75-0161), with no traces of secondary peaks. This indicates that $MgMnO_{3-\delta}$ is chemically inert and stable in the presence of the GDC promoter, even at the high temperature of 1300 °C. Therefore, we anticipate no phase change problems when using the $MgMnO_{3-\delta}$ -GDC composites as oxygen transfer materials at the operation temperature of 900 °C.

The conversion ratios of the oxygen carrier material (X_{red} or X_{ox}) are defined by the following equations and can be used to evaluate the degree of reduction or oxidation.

$$X_{red} = \frac{m_{ox} - m}{m_{ox} - m_{red}} \quad (4)$$

$$X_{ox} = \frac{m - m_{red}}{m_{ox} - m_{red}} \quad (5)$$

Here, m is the mass of the sample at a given time, m_{ox} is the fully oxidized mass, and m_{red} is the fully reduced mass. The oxygen transfer capacity (R_{OTC}) is an index indicating how much oxygen can be delivered from the

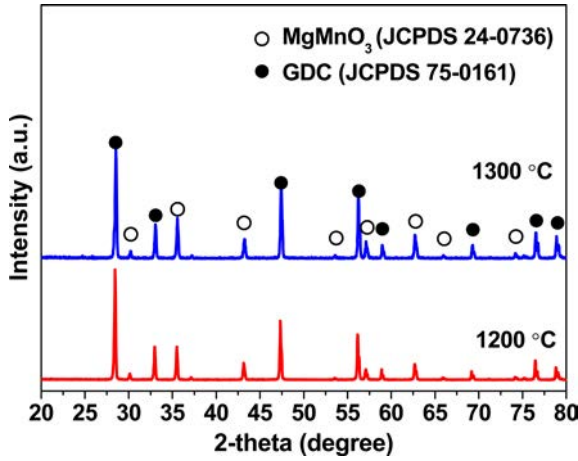


Fig. 1. XRD patterns of $\text{MgMnO}_{3-\delta}$ -GDC composites fired in air at 1200 and 1300 °C for 3 hrs.

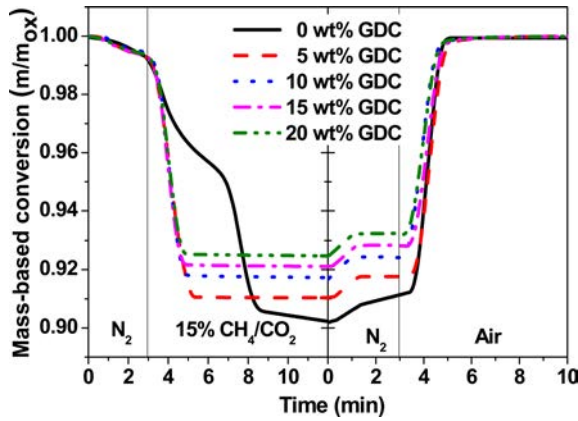


Fig. 2. Redox curves of the fifth redox cycles of $\text{MgMnO}_{3-\delta}$ -GDC composites at 900 °C.

oxygen carrier material to react with fuel; it is defined as follows.

$$R_{OTC} = \frac{m_{ox} - m_{red}}{m_{ox}} \quad (6)$$

The higher the oxygen transfer capacity, the less oxygen carrier material is required in the reactor, thereby reducing the operation cost of the process.

Re-dox curves of $\text{MgMnO}_{3-\delta}$ -GDC composites obtained during the fifth cycle of TGA at 900 °C are shown in Fig. 2. As the oxygen in the oxygen carrier material is released and reacts with CH_4 during the reduction reaction, the mass of the sample decreases. During the oxidation reaction, oxygen in the air binds with the reduced oxygen carrier material and increases their mass. Interestingly, during the 3 min of nitrogen flow between steps, there was a slight decrease in weight, which we attributed to the chemical looping oxygen uncoupling (CLOU) characteristic of $\text{MgMnO}_{3-\delta}$. CLOU is a phenomenon whereby lattice oxygen escapes from the oxygen carrier material under heating [16].

The weight gain observed during oxidation was

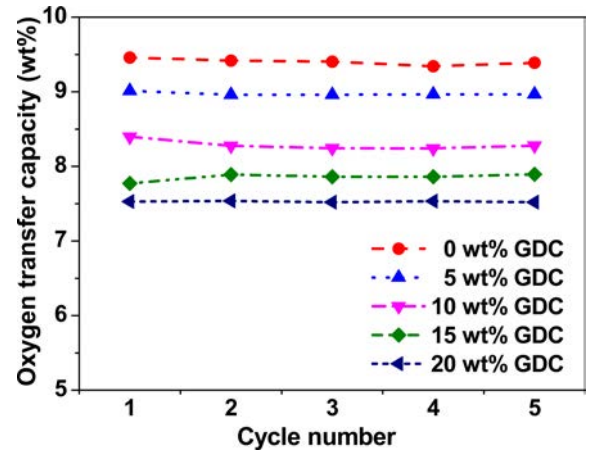


Fig. 3. Oxygen transfer capacities of $\text{MgMnO}_{3-\delta}$ -GDC composites at 900 °C versus redox cycle number.

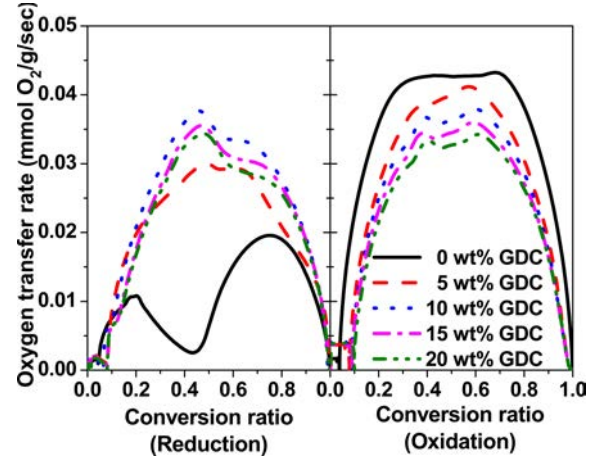


Fig. 4. Oxygen transfer rates of $\text{MgMnO}_{3-\delta}$ -GDC composites during the 5th redox cycle.

observed to be equal to the weight loss during reduction, indicating that the re-dox reaction was reversible. The oxygen transfer capacities of $\text{MgMnO}_{3-\delta}$ -GDC composites having the GDC contents of 0, 5, 10, 15, and 20 wt% were measured to be 9.4, 9.0, 8.3, 7.9, and 7.5 wt%, respectively. The oxygen transfer capacities of $\text{MgMnO}_{3-\delta}$ -GDC composites decreased with increasing GDC because the relative amount of $\text{MgMnO}_{3-\delta}$ participating in the reduction reaction decreased. Actually, the theoretical oxygen transfer capacities of $\text{MgMnO}_{3-\delta}$ -GDC composites having the GDC contents of 5, 10, 15, and 20 wt% were 8.9, 8.5, 8.0, and 7.5 wt%, respectively, which were similar to the empirical oxygen transfer capacities.

Fig. 3 shows the oxygen transfer capacity retention of $\text{MgMnO}_{3-\delta}$ -GDC composite at 900 °C during repeated re-dox cycling. No degradation of oxygen transfer capacity was observed during the re-dox cycles. It is well known that the oxygen transfer capacity decreases with continued re-dox cycling due to phase transition. Moreover, GDC did not affect the oxygen transfer

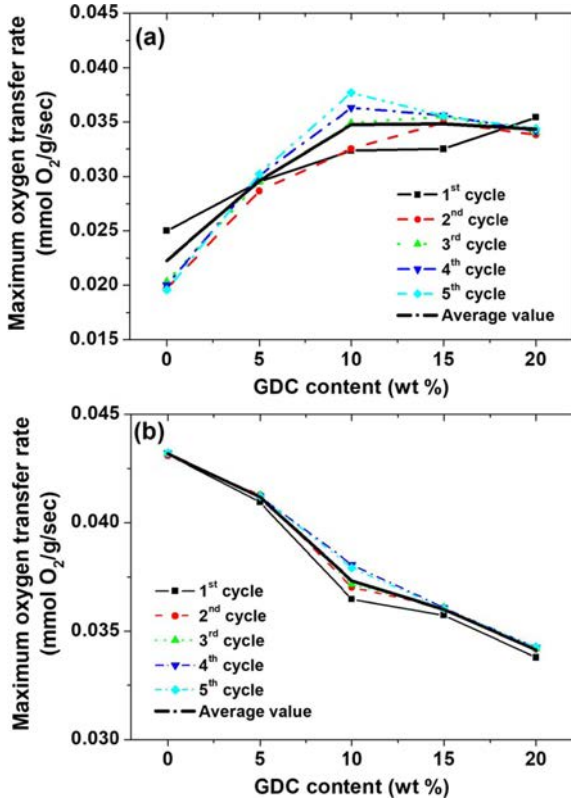


Fig. 5. Maximum oxygen transfer rate of $MgMnO_{3-\delta}$ -GDC composites versus GDC content for the (a) reduction and (b) oxidation reactions.

property of $MgMnO_{3-\delta}$ during the re-dox cycle. Recall that $MgMnO_{3-\delta}$ maintained its phase and crystal structure after firing with GDC (Fig. 1).

The oxygen transfer rate, referring to the amount of oxygen consumed per unit time and weight [mmol-O₂/g/s], can be calculated from TGA data. Fig. 4 shows the oxygen transfer rate of $MgMnO_{3-\delta}$ -GDC composites during the re-dox reaction versus the conversion ratio, calculated from the slopes of the mass change profiles in Fig. 2. In the case of $MgMnO_{3-\delta}$ without GDC, the oxygen transfer rate for the oxidation reaction was clearly noted to be about two times as fast as that for the reduction reaction. Similarly, it has been reported that the rate index of $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ for O₂ as the reacting gas is four times higher than that for CH₄ as the reacting gas [13]. Interestingly, the oxygen transfer rate for the reduction reaction increased significantly for the composite including 5 wt% GDC, and the difference between the oxygen transfer rates for the reduction and oxidation reactions decreased with increasing GDC content. This suggests that GDC may affect the reaction kinetics of $MgMnO_{3-\delta}$ -GDC composites, especially in its reduction by CH₄ gas.

Since the re-dox reaction of oxygen carrier material takes place through the several steps of gas diffusion, surface chemisorption, charge transfer, and bulk diffusion, the individual kinetics at any step could be

the rate-determining step of the whole reaction. The maximum oxygen transfer rates of $MgMnO_{3-\delta}$ -GDC composites in the reduction and oxidation reaction are plotted in Fig. 5 for various GDC contents. The oxygen transfer rate in the reduction reaction increased with increasing GDC content up to 10 wt% GDC and then was saturated (Fig. 5(a)). It is well known that GDC has oxygen storage capability due to its oxygen vacancies, and GDC has thus been widely used as a catalyst [17, 18]. To verify the oxygen storage characteristics of GDC, temperature-programmed oxidation analysis of a pristine GDC sample not subjected to reduction treatment and of a GDC sample reduced by 5% H₂/Ar was performed; the reduced GDC samples showed much greater weight gain than the pristine GDC samples (Fig. 6), and thus showed more oxygen vacancies in the reducing atmosphere. GDC can adsorb oxygen on its surface and store oxygen in its lattice because many oxygen vacancies exist on its surface. When GDC is exposed to a reducing atmosphere, its Ce⁴⁺ is reduced to Ce³⁺, accompanied by the formation of oxygen vacancies to neutralize the charge. Consequently, the concentration of oxygen vacancies on the surface increases and the oxygen storage capability can be further improved by exposure to a reducing atmosphere.

Generally, it has been reported that the surface adsorption of the reaction gas improves as the amount of oxygen vacancies on the surface increases. Therefore, the improvement in the oxygen transfer rate of $MgMnO_{3-\delta}$ -GDC composites for the reduction reaction realized by the addition of GDC arises from increased surface adsorption of CH₄, which is a reaction gas, via the oxygen vacancies formed on the surface of the GDC. Meanwhile, the observation that the reduction reaction rate becomes saturated for GDC content over 10 wt% can be explained by Kusy's percolation theory. Percolations are commonly used to describe the conduction properties of composites in terms of fluid movement through porous materials [19]. In composite materials, the volume fraction or the degree of contact between the matrix and the dispersed phase leads to a discrete change in the properties of the entire material. That is to say, when a percolation is formed, the phases are continuously connected. The threshold of the percolation is expressed as follows.

$$V_c = 100 \left[1 + \left(\frac{\Phi}{4X_c} \right) \left(\frac{R_p}{R_m} \right) \right]^{-1} \quad (7)$$

Here, V_c is the critical volume fraction, Φ is the reciprocal of the planar packing factor, R_p is the radius of the primary particle ($MgMnO_{3-\delta}$), R_m is the radius of the dispersed particle (GDC), and X_c is the critical fraction of the surface of each primary particle covered by a dispersed particle. We assumed that the GDC particles were packed in a cubic manner in the composite matrix, and that, for cubic packing, $\Phi = 1.27$

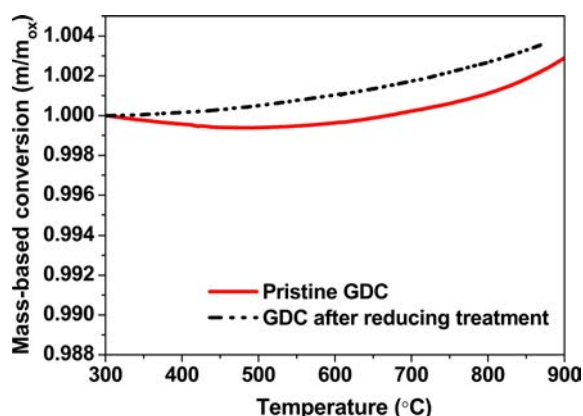


Fig. 6. Temperature-programmed oxidation data of pristine GDC without reducing treatment and of GDC reduced by 5% H₂/Ar.

and $X_c = 0.42$. Particle sizes of MgMnO_{3-δ} and GDC were 5 and 0.025 μm, respectively, as measured using FE-SEM. Based on Kusy's percolation theory, the calculated percolation threshold of GDC in the MgMnO_{3-δ} matrix was 9.7 wt%. Therefore, for GDC contents of approximately 10 wt% or greater, GDC particles become connected to each other rather than being directly adjacent to MgMnO_{3-δ} only, such that further increases in GDC content do not enhance the reduction reaction of MgMnO_{3-δ}.

Contrastingly, the oxygen transfer rates of MgMnO_{3-δ}-GDC composites during the oxidation reaction decreased linearly with increasing GDC content (Fig. 5(b)). This is due to the oxygen storage properties of GDC. In the case of the reduction reaction, CH₄ adsorbs on the oxygen vacancies on the surface of GDC and then is transferred to MgMnO_{3-δ}, thereby promoting the reduction reaction. However, in the oxidation reaction, oxygen molecules adsorbed on the oxygen vacancies are preferentially inserted into the GDC lattice, representing oxygen storage rather than reaction.

Conclusions

The present study investigated the effect of Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) as a promoter of the oxygen transfer properties of MgMnO_{3-δ}-GDC composite oxygen carrier materials for CLC. The GDC promoter was chemically stable and did not react with the MgMnO_{3-δ} to form secondary phases, even at the high temperature of 1300 °C. Whereas MgMnO_{3-δ} was reduced to (Mg,Mn)O during the reaction with CH₄, GDC very stably remained in its initial phase. Therefore, the oxygen transfer capacity of MgMnO_{3-δ}-GDC composites decreased with increasing GDC content. However, increasing GDC content considerably increased the oxygen transfer rate in the reduction reaction, which we attribute to an increase in the surface adsorption of CH₄ via the oxygen vacancies formed on the surface of the GDC. Interestingly, the

oxygen transfer rate for the reduction reaction increased with increasing GDC content up to 10 wt%, and was then saturated. This phenomenon could be explained by Kusy's percolation theory. Contrastingly, the oxygen transfer rate for the oxidation reaction decreased linearly with increasing GDC content due to oxygen storage by GDC. Nevertheless, the oxygen transfer rate of the MgMnO_{3-δ}-GDC composite during the oxidation reaction was comparable to that of pristine MgMnO_{3-δ}. In conclusion, GDC affects the reaction kinetics of MgMnO_{3-δ}-GDC composites, and the optimum amount of GDC as a promoter is 10 wt%, considering the trade-off between oxygen transfer capacity and oxygen transfer rate.

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