



# Reliable oxygen transfer in $\text{MgAl}_2\text{O}_4$ spinel through the reversible formation of oxygen vacancies by $\text{Cu}^{2+}/\text{Fe}^{3+}$ anchoring

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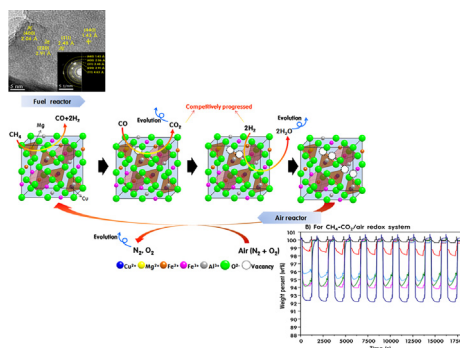


## HIGHLIGHTS

- $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_y\text{Al}_{2-y}\text{O}_4$  spinel structured oxygen carriers were successfully prepared.
- Reversible oxygen vacancies were observed in a  $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_y\text{Al}_{2-y}\text{O}_4$  spinel structure.
- $\text{CH}_4$  and  $\text{CO}$  gases were much adsorbed on the surface of  $\text{Cu}_{0.75}\text{Mg}_{0.25}\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_4$  spinel particle.
- The greatest oxygen transfer in  $\text{Cu}_{0.75}\text{Mg}_{0.25}\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_4$  particle was obtained.

## GRAPHICAL ABSTRACT

Reliable oxygen transfer in  $\text{MgAl}_2\text{O}_4$  spinel through the reversible formation of oxygen vacancies by  $\text{Cu}^{2+}/\text{Fe}^{3+}$  anchoring.



## ARTICLE INFO

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Oxygen vacancy

## ABSTRACT

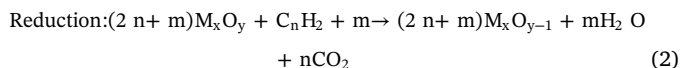
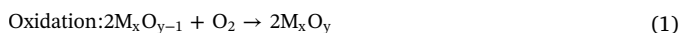
This study focused on  $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_y\text{Al}_{2-y}\text{O}_4$  oxygen carriers for application in the chemical looping combustion of methane.  $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_y\text{Al}_{2-y}\text{O}_4$  was fabricated by simultaneously substituting  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  with  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  in the spinel structure of  $\text{MgAl}_2\text{O}_4$ . As a result, a great synergistic effect was observed:  $\text{Cu}_{0.75}\text{Mg}_{0.25}\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_4$  exhibited 7.85% oxygen transfer capacity in the  $\text{CH}_4\text{-CO}_2$ /air redox system. Methane and carbon monoxide were significantly adsorbed on the surface of the  $\text{Cu}_x\text{Mg}_{1-x}\text{Fe}_y\text{Al}_{2-y}\text{O}_4$  particles. Cyclic voltammetry studies predicted the active lifetime of the oxygen carrier, which had not been reported until now.  $\text{Cu}_{0.75}\text{Mg}_{0.25}\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_4$  was expected to exhibit the greatest oxygen transfer capacity after 300 redox cycles and maintain an oxygen transfer efficiency of 92% until the 1000th redox cycle in the  $\text{H}_2\text{-N}_2$ /air redox system. This study concluded that the active metal species, containing  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions, were stably anchored in the spinel structure; this led to the reversible formation of oxygen vacancies in the spinel structure, resulting in an excellent oxygen transfer capacity that could be maintained for a long time.

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## 1. Introduction

The chemical looping combustion (CLC) technology has the advantages of NO<sub>x</sub> reduction and CO<sub>2</sub> source separation compared to the conventional combustion method in which the fuel is directly contacted with air. It is considered a new combustion/power generation technology that is capable of preventing air pollution and regulating CO<sub>2</sub> emission [1]. The setup for CLC is composed of an air reactor where oxidation occurs and a fuel reactor where reduction is performed [2,3]. Oxygen carrier particles circulate between the two reactors to transfer oxygen from the air reactor to the fuel reactor.



In the air reactor, metal particles are oxidized by oxygen from the air to form metal oxides, which are then transferred to the fuel reactor, as shown in Eq. (1). In the fuel reactor, the metal oxides react with a fuel (e.g., CH<sub>4</sub>, H<sub>2</sub>, CO, C<sub>n</sub>H<sub>2+m</sub>, natural gas, coal, biomass, etc.) to form metal particles and generate CO<sub>2</sub> and H<sub>2</sub>O, as shown in Eq. (2). The reduced metal particles formed in the fuel reactor are recycled to the air reactor, and the above process is repeated. Because the gaseous products only consist of CO<sub>2</sub> and H<sub>2</sub>O vapor, highly concentrated CO<sub>2</sub> can be separated from the process by condensing and removing the water vapor [4,5]. Although the oxygen carrier particles do not achieve 100% oxidation, only N<sub>2</sub> and O<sub>2</sub> are emitted during this reaction that do not cause environmental problems. However, in the reduction reaction, even when a small amount of gaseous fuel is discharged, the separation of CO<sub>2</sub> from the gaseous fuel is difficult; hence, the conversion rate of the fuel should be high. Therefore, most studies on the reactivity of oxygen carriers have mainly focused on the reduction reactions [6,7]. Oxygen carrier capacity can be considered as the most important characteristic that determines the reduction reactivity of oxygen carriers. The oxides of first-row transition metals such as Mn, Fe, Co, Ni, and Cu are good candidates for oxygen carriers because they have high lattice oxygen reactivity and high oxygen-carrying capacity [8–12]. Recently, bimetallic active oxygen carriers have been introduced, for example, Fe-Mn, Co-Mn, Ni-Mn, Cu-Mn, Cu-Fe, Cu-Ni, Ni-Fe, Ni-Co, etc. [13–20]. Additionally, to ensure that mono-metal active oxygen carriers exhibit good mechanical strengths and stable performances during sustained operation, the active metal oxides have been stabilized by catalyst supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub> [21–25]. In particular, Al<sub>2</sub>O<sub>3</sub> has been widely used as support; however, the formation of aluminates spinel structures of NiAl<sub>2</sub>O<sub>4</sub>, CuAl<sub>2</sub>O<sub>4</sub>, and FeAl<sub>2</sub>O<sub>4</sub> at high temperature reduces the activity of the oxygen carriers [26–28]. To mitigate spinel formation from Al<sub>2</sub>O<sub>3</sub>, researchers have proposed the addition of alkali or alkaline earth metal oxides such as MgO or CaO to form more stable aluminates such as MgAl<sub>2</sub>O<sub>4</sub> or CaAl<sub>2</sub>O<sub>4</sub> to inhibit the interactions between Al<sub>2</sub>O<sub>3</sub> and the active metal oxides [29,30].

Our previous study confirmed that Cu has a very good oxygen transfer capacity [24], but elemental Cu melts at relatively low temperatures. Nonetheless, Cu-Fe as a bimetallic oxide oxygen carrier has attracted much interest due to its low cost. Cu and Fe are however highly dense at high temperatures, and Cu still needs to be stabilized by melting. Scheme 1 shows both the purpose and the originality of this study and visually compares the mechanisms of crystal growth by sintering between active metal particles during repetitive redox cycles at high temperature (A) and that of crystal growth inhibition by anchoring active metal particles (B). Two Cu and Fe oxide species were safely anchored into a spinel-structured support to prevent sintering at high temperature. Generally, the strong sintering formed between the active species such as Cu-Cu, Fe-Fe, or Cu-Fe accelerates active deterioration [17]. Inhibiting the sintering process can eventually lead to a sustained oxygen delivery capability. Moreover, this technique can also reduce

the loss of active species exposed to particles resulting from collisions between particles during the long-term redox reaction cycle.

Therefore, this study aims at investigating the oxygen transfer capacity of spinel-structured Cu<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>y</sub>Al<sub>2-y</sub>O<sub>4</sub> particles formed by substituting the Mg and Al ions in the framework of the MgAl<sub>2</sub>O<sub>4</sub> spinel particle with Cu and Fe ions via the so-called *anchoring effect*. The oxygen transfer capacity of the novel structure is obtained with gaseous CH<sub>4</sub> and CO<sub>2</sub>, and this study will attempt to estimate the lifetime of the oxygen carriers through cyclic voltammetry, which is a novel approach that has not yet been attempted.

## 2. Material and methods

### 2.1. Synthesis of Cu<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>y</sub>Al<sub>2-y</sub>O<sub>4</sub> particles

To understand the oxygen transfer capacities of the Cu and Fe ions, we first synthesized MgAl<sub>2</sub>O<sub>4</sub> as a basic starting particle and, in a subsequent step, MgFeAlO<sub>4</sub>, in which 50 mol.% of the Al<sup>3+</sup> ions was substituted by Fe<sup>3+</sup>. In addition, Cu<sub>0.5</sub>Mg<sub>0.5</sub>Al<sub>2</sub>O<sub>4</sub> was fabricated by substituting 50 mol.% of Mg<sup>2+</sup> by Cu<sup>2+</sup>, and Cu<sub>0.5</sub>Mg<sub>0.5</sub>FeAlO<sub>4</sub> was synthesized by simultaneously substituting 50 mol.% of Mg<sup>2+</sup> and Al<sup>3+</sup> by 50 mol.% of Cu<sup>2+</sup> and Fe<sup>3+</sup>, respectively. In the final step, Mg<sup>2+</sup> and Al<sup>3+</sup> were substituted by 75 mol.% of Cu<sup>2+</sup> and Fe<sup>3+</sup> to form Cu<sub>0.75</sub>Mg<sub>0.25</sub>Al<sub>2</sub>O<sub>4</sub> and Cu<sub>0.75</sub>Mg<sub>0.25</sub>Fe<sub>1.5</sub>Al<sub>0.5</sub>O<sub>4</sub> to further investigate the effects of Cu<sup>2+</sup> and Fe<sup>3+</sup> in the oxygen carriers. Consequently, six compositional particles were designed using the conventional sol-gel process: MgAl<sub>2</sub>O<sub>4</sub>, MgFeAlO<sub>4</sub>, Cu<sub>0.5</sub>Mg<sub>0.5</sub>Al<sub>2</sub>O<sub>4</sub>, Cu<sub>0.5</sub>Mg<sub>0.5</sub>FeAlO<sub>4</sub>, Cu<sub>0.75</sub>Mg<sub>0.25</sub>Al<sub>2</sub>O<sub>4</sub>, and Cu<sub>0.75</sub>Mg<sub>0.25</sub>Fe<sub>1.5</sub>Al<sub>0.5</sub>O<sub>4</sub>.

In a typical synthesis, pre-calculated amounts of divalent metal chloride (MCl<sub>2</sub>·xH<sub>2</sub>O, M = Cu and Mg, 99.9%, Junsei Co, Japan) and trivalent metal chloride (MCl<sub>3</sub>·xH<sub>2</sub>O, M = Fe and Al, 99.9%, Junsei Co, Japan) as metal precursors were added to 500 mL of distilled water. Then, NH<sub>4</sub>OH (99%) was added dropwise into the solution to maintain a pH of 11.0, and the final solution was vigorously stirred for 24 h at room temperature. The molar composition of Cu, Mg, Fe, and Al was varied, and the maximum concentration of Cu<sup>2+</sup> and Fe<sup>3+</sup> was 75 mol.% of the total amount of Mg<sup>2+</sup> and Al<sup>3+</sup>, respectively. The resulting suspension was evaporated at 80 °C for 24 h, the dried powder was pelletized at a pressure of 300 kgfcm<sup>-2</sup> and finally heat-treated at 1100 °C for 10 h to induce its crystallization into a spinel structure. For the redox cycling tests, the obtained sample was crushed and sieved between 45 and 180 μm. For the purpose of this study, the term “anchor” will be used interchangeably with the terms “insert” and “substitute” although it may not be scientifically appropriate.

### 2.2. Characterization of Cu<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>y</sub>Al<sub>2-y</sub>O<sub>4</sub> particles

The chemical and physical properties of the Cu<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>y</sub>Al<sub>2-y</sub>O<sub>4</sub> oxygen carrier particles were measured through various experiments. The crystal structure, morphology, particle size, and atomic composition/elemental distribution of the prepared Cu<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>y</sub>Al<sub>2-y</sub>O<sub>4</sub> particles were studied through powder X-ray diffraction (XRD; model MPD from PANalytical, Netherland) using nickel-filtered CuKα radiation (30.0 kV, 30.0 mA) over the 2θ range 10–100°, high-resolution transmission electron microscopy (TEM; 120 kV, H-7600, Hitachi, Japan), scanning electron microscopy (SEM; S-4100, 15 kV, Hitachi, Japan), and energy dispersive X-ray spectroscopy/element image mapping analysis (EDS; EX-250, 15 kV, Horiba, Japan).

The typical survey and high-resolution quantitative X-ray photoelectron spectroscopy (XPS; AlKα, 1486.6 eV, Thermo scientific, UK) patterns were analyzed to determine the changes in the oxidation states of the Cu and Fe ions during the redox reaction. To investigate the oxygen transfer and redox processes of the metals during the redox cycling test, XPS measurements were performed on the Cu<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>y</sub>Al<sub>2-y</sub>O<sub>4</sub> particles before and after the redox cycling tests. The Cu<sub>3d</sub>, Mg<sub>2p</sub>, Fe<sub>3d</sub>, Al<sub>2p</sub>, and O<sub>1s</sub> binding energies of Cu<sub>x</sub>Mg<sub>1-x</sub>Fe<sub>y</sub>Al<sub>2-y</sub>O<sub>4</sub> were

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