



## Synergetic effects of mixed copper–iron oxides oxygen carriers in chemical looping combustion

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### HIGHLIGHTS

- ▶ The components of CuO–Fe<sub>2</sub>O<sub>3</sub> oxygen carrier were optimized to obtain good reactivity and physical stability.
- ▶ Synergistic effect of CuO–Fe<sub>2</sub>O<sub>3</sub> was observed and characterized for chemical looping reaction.
- ▶ The nature of the fuel influences the reactivity and reduction status of the oxygen carriers.
- ▶ Possible reasons for the deeper reduction of Fe<sub>2</sub>O<sub>3</sub> in the presence of CuO are presented.

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### ABSTRACT

Chemical looping combustion (CLC) is an emerging technology for clean energy production from fuels. CLC produces sequestration-ready CO<sub>2</sub>-streams without a significant energy penalty. Development of efficient oxygen carriers is essential to successfully operate a CLC system. Copper and iron oxides are promising candidates for CLC. Copper oxide possesses high reactivity but it has issues with particle agglomeration due to its low melting point. Even though iron oxide is an inexpensive oxygen carrier it has a slower reactivity. In this study, mixed metal oxide carriers containing iron and copper oxides were evaluated for coal and methane CLC. The components of CuO and Fe<sub>2</sub>O<sub>3</sub> were optimized to obtain good reactivity while maintaining physical and chemical stability during cyclic reactions for methane-CLC and solid-fuel CLC. Compared with single metal oxygen carriers, the optimized Cu–Fe mixed oxide oxygen carriers demonstrated high reaction rate, better combustion conversion, greater oxygen usage and improved physical stability.

Thermodynamic calculations, XRD, TGA, flow reactor studies and TPR experiments suggested that there is a strong interaction between CuO and Fe<sub>2</sub>O<sub>3</sub> contributing to a synergistic effect during CLC reactions. The amount of oxygen release of the mixed oxide carrier in the absence of a fuel was similar to that of the single metal oxides. However, in the presence of fuels, the oxygen consumption and the reaction profiles of the mixed oxide carriers were significantly better than that of the single metal oxides. The nature of the fuel not only influenced the reactivity, but also the final reduction status of the oxygen carriers during chemical looping combustion. Cu oxide of the mixed oxide was fully reduced metallic copper with both coal and methane. Fe oxide of the mixed oxide was fully reduced Fe metal with methane but it was reduced to only FeO with coal. Possible mechanisms of how the presence of CuO enhances the reduction of Fe<sub>2</sub>O<sub>3</sub> are discussed.

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### 1. Introduction

Capturing CO<sub>2</sub> from power plants that use fossil fuels is one of several strategies to reduce global CO<sub>2</sub> emissions. The task of removing CO<sub>2</sub> from power plant flue gas is challenging because existing methods to separate CO<sub>2</sub> from the gas mixture requires a significant portion of power plant output. The separation task

can be simplified by replacing conventional air with pure oxygen so that the products from this combustion are just CO<sub>2</sub> and water that could be easily separated by condensation. However, current commercial techniques for producing oxygen from air require very energy-intensive cryogenic processes. Chemical looping combustion (CLC) is a novel combustion technology [1–3] that utilizes an oxygen carrier, such as metal oxide, to transport oxygen from air to fuel, thereby avoiding direct contact between fuel and air. The significant advantage of CLC over conventional combustion is that CLC can produce a sequestration-ready CO<sub>2</sub> stream—not diluted by

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nitrogen (N<sub>2</sub>)—without expending any major energy required for the separation of CO<sub>2</sub>. The overall CLC process, in which the metal oxide cycles between oxidized and reduced states, is exothermic.

Development of efficient oxygen carriers is essential to successfully operate a CLC system. Various oxygen carriers composed of metal oxides and supports [4–21] have been tested with gaseous methane or solid coal as the fuels. It is generally accepted that Ni, Cu, and Fe oxides possess sufficient activity for a CLC system among the transient metal oxides. Nickel oxide has been studied in greater detail than other transitional metal oxides because it has more favorable characteristics for methane chemical looping combustion [22–24]. Recently, NiO/NiAl<sub>2</sub>O<sub>4</sub> oxygen carriers were tested in a 10-kw reactor for 160 h with approximately 99% conversion [25,26]; however, a major drawback of NiO-based oxygen carriers is associated health and environmental issues.

The literature reports limited work on mixed-metal oxides as oxygen carriers. Perovskite-type compounds (such as La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub>) [27] have been reported for their ability to release oxygen without major chemical or physical changes in the bulk phases, but the application of these compounds in CLC systems may not be feasible due to expensive production cost and low oxygen capacity. Bimetallic compounds (such as Co–Ni/Al<sub>2</sub>O<sub>3</sub> and Fe–Mn oxides) have been evaluated as oxygen carriers in the past [28,29]. It was found that Co–Ni/Al<sub>2</sub>O<sub>3</sub> samples displayed high reactivity and stable behavior over multiple reduction–oxidation experiments. Ryden et al. concluded that combined oxides of iron and manganese have very favorable thermodynamic properties and could potentially be suitable for CLC applications [30]. However, they also found that the examined material exhibited low physical stability, which could be improved by the addition of inert material. In our previous work [31], we investigated a supported Fe–Mn oxide mixture for chemical looping combustion using coal synthesis gas for fuel. The addition of Mn oxides exhibited a positive effect on the chemical stability of Fe<sub>2</sub>O<sub>3</sub> multi-cycle CLC reactions at 900 °C. We also observed that the support had a significant effect on both fractional reduction–oxidation and reaction rate. Recently, CuFe<sub>2</sub>O<sub>4</sub> was studied for CLC with coal using TGA [32] and the tests were limited to two cycles due to difficulties in sample handling. The results indicated two combustion reactions mechanisms: at 300–600 °C, CuFe<sub>2</sub>O<sub>4</sub> was rapidly reduced to Cu and Fe<sub>3</sub>O<sub>4</sub> by transfer/combustion of lattice oxygen in CuFe<sub>2</sub>O<sub>4</sub>; the formed Fe<sub>3</sub>O<sub>4</sub> was further reduced to Fe<sub>2.962</sub>O<sub>4</sub> at 600–850 °C, especially above 800 °C. CuFeO<sub>2</sub> and CuO<sub>2</sub> were formed through direct decomposition of CuFe<sub>2</sub>O<sub>4</sub>. A strong interaction was also observed between Cu–Fe mixed oxides with coal ash, resulting in the formation of iron silicates. Moghtaderi et al. conducted both experimental and theoretical studies to understand the reactivity of H<sub>2</sub>, CO and CH<sub>4</sub> with binary mixtures of CuO, Fe<sub>2</sub>O<sub>3</sub> and NiO [33]. It was found that the reaction parameters of the binary mixtures can be calculated directly using the kinetic parameters of the parent materials. Wang et al. have conducted bench-scale reactor tests of chemical looping combustion with a MgAl<sub>2</sub>O<sub>4</sub> supported Fe<sub>2</sub>O<sub>3</sub>–CuO mixture and coke oven gas [34]. The optimized oxide composition contained 45 wt% Fe<sub>2</sub>O<sub>3</sub> and 15%CuO supported on 40%MgAl<sub>2</sub>O<sub>4</sub>. Their data indicated that higher temperature has a positive effect on reaction performance. Particle breakage and CuO sintering were observed on the used sample after 15 h of fluidized-bed recirculation. The maximum fuel conversion of the CuO–Fe<sub>2</sub>O<sub>3</sub> mixture can reach up to 92%. TiO<sub>2</sub> supported CuO–Fe<sub>2</sub>O<sub>3</sub> mixtures have also been investigated on coal CLC in TGA [34], and have displayed improved reactivity. SEM images after one cycle tests proved significant agglomeration at 950–1000 °C. Thus, the optimum temperature recommended for CuO–Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> carriers by coal CLC was 900 °C.

Fe<sub>2</sub>O<sub>3</sub> and CuO were chosen in this study for developing oxygen carrier materials to obtain high reactivity and stable reaction

performance, and to address cost and environmental concerns. Previous work on methane CLC demonstrated that reduction rates for the reaction from Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> are fast, but the subsequent reduction to FeO is very slow [35]. Samples prepared by impregnation of 80%Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> are reported to possess stable reactivity in 20-cycle TGA tests with methane conversions between 85% and 94% [36,37]. Although its redox rates are slower than that of CuO or NiO, Fe<sub>2</sub>O<sub>3</sub> is still considered an attractive option for CLC application because of its low cost and environmental compatibility. CuO has several favorable features including high reactivity, favorable thermodynamic properties for complete conversion of gaseous hydrocarbon fuels (e.g. methane), and relative low material cost compared with other transition metal oxygen carrier materials, such as Ni, Mn, or Co. However, pure Cu metal has a fairly low melting point (1083 °C), which may introduce severe particle agglomeration and surface sintering during multiple CLC reaction cycles.

The objectives of this work were to design an oxygen carrier with optimized CuO and Fe<sub>2</sub>O<sub>3</sub> composition to achieve high reactivity and great stability, and to examine detailed reaction mechanisms for both coal CLC and methane CLC. Extensive CLC studies with Cu–Fe mixtures have not been reported in the past specifically with methane as the fuel. Alumina or bentonite, were used as supports/binders to avoid particle agglomeration and enhance the reactivity and durability of CuO and Fe<sub>2</sub>O<sub>3</sub> mixtures. Extra CuO was present in most compositions to maximize reactivity. The oxygen carriers were prepared with different methods and their reaction performances were evaluated using TGA and bench-scale fixed-bed flow reactors. For comparison, the performance of bentonite-supported monometallic CuO and Fe<sub>2</sub>O<sub>3</sub> were also evaluated. Thermodynamic calculations, SEM and XRD were conducted to understand the phase changes during CLC reactions.

## 2. Materials and methods

### 2.1. Oxygen carrier preparation

In this study, the oxygen carrier was prepared using several methods:

- Physical mixing method:* Pure CuO (Sigma–Aldrich, >99.8%, <5 μm), Fe<sub>2</sub>O<sub>3</sub> (Sigma–Aldrich, >98%, <5 μm) and Al<sub>2</sub>O<sub>3</sub> (fused powder, primarily α-phase, ~44 μm) supports were mixed thoroughly, and deionized water was added to the powder mixture to obtain a paste. The paste was dried at room temperature for 24 h. The dried material was then calcined at 900 °C in air for 8 h. The calcined sample was crushed and sieved into smaller particles with an average size of 100 μm.
- Liquid impregnation method:* Nitrates of copper (Alfa-aeser, >98%) and iron (Alfa-aeser, >98%) were dissolved in the desired amount water, and mixed thoroughly. The solution was added by drops to an Al<sub>2</sub>O<sub>3</sub> support while stirring. The impregnation–calcination process was conducted twice to obtain the desired metal oxide loadings. The paste was dried at room temperature for 24 h and calcined at 900 °C in air for 8 h. The calcined sample was crushed and sieved into smaller particles with an average size of 100 μm.
- Co-precipitation method:* Nitrates of copper, iron and aluminum (Alfa-aeser, >98%) were mixed and dissolved in water. Then ammonia was added by drops while stirring until all metal hydroxides were fully precipitated. The solid precipitate was filtered and the paste was dried at room temperature for 24 h and calcined at 900 °C in air for 8 h. The calcined sample was crushed and sieved into smaller particles with an average size of 100 μm.

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