Ferrites as redox catalysts for chemical looping processes

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HIGHLIGHTS

- $CuFe_2O_4$ can deliver the highest amount of lattice O and regain it in air.
- $CuFe_2O_4$ has the highest reactivity towards CH_4 and is stable after 5 redox cycles.
- $NiFe_2O_4$ and $ZnFe_2O_4$ are initially very active, however they deactivate very fast.
- $MnFe_2O_4$ has low reactivity with CH_4 and low Oxygen Transfer Capability.
- $CoFe_2O_4$, has moderate initial reactivity, however it presents remarkable stability.

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ABSTRACT

Spinel ferrites can accommodate oxygen vacancies in their structure and reversibly exchange oxygen with the environment at high temperatures, depending on the partial pressure of oxygen. Therefore their use in Chemical Looping Combustion (CLC) is being studied intensively. In the present work the use of ferrites with the general formula of $MeFe_2O_4$ (Me = Mn, Ni, Zn, Co, Cu) as oxygen carriers or potentially reactive supports for oxygen carriers in Chemical Looping Combustion is explored. Polycrystalline ferrite samples are prepared using the conventional ceramic technology of "solid-state reaction". The performance of the prepared materials is evaluated at a fixed-bed laboratory scale pulse reaction unit. During the fuel oxidation step, methane pulses are injected over the ferrite powder while subsequent oxidation of the solid is performed with gaseous oxygen. The performance of the candidate materials is ranked by comparing the amount of oxygen per mole solid (δ) that can be delivered reversibly to the fuel which corresponds to the Oxygen Transfer Capacity of the different ferrite materials as well as the methane conversion during the fuel oxidation step and the gaseous product distribution. The stability of the materials during multiple reduction–oxidation cycles is evaluated during 5–10 subsequent cycles, each of which is comprised of an activation–regeneration and a solid oxidation step. All the examined ferrites have the ability to deliver their lattice oxygen to a fuel and to some extend regain it in the presence of air. Cu ferrites are very active in CH_4 oxidation with maximum conversion higher than 95%, while Zn and Ni ferrites are also highly ranked with methane conversion reaching up to 90% and 78% respectively, however they deactivate very fast after redox cycles. Mn ferrites present relatively low activity ($\sim$30%), while Co ferrites present moderate methane conversion, approximately 68% but remarkable stability during subsequent redox cycles. Cu-, Co- and Ni-ferrites can deliver higher amounts of lattice O, compared to Mn ferrite. The structural and morphological stability of the materials after the multiple redox cycles is examined by X-ray diffraction and SEM–EDS analysis.

1. Introduction

Concern about the global climate change prompted research on reducing CO_2 emissions during fossil fuel combustion. Existing CO_2 capture technologies, based on post-combustion separation, are expensive and energy intensive, thus reducing the overall efficiency of a power plant. Chemical Looping Combustion (CLC) is a novel combustion technology [1–4] that has been suggested as an energy-efficient method for capturing CO_2 during fuel combustion. It involves the use of an oxygen carrier, such as a metal oxide, which transports oxygen from the air to the fuel, thereby

avoiding direct contact between fuel and air. The CLC system comprises of two reactors, a fuel reactor and an air reactor with the oxygen carrier continuously circulating between them. In the fuel reactor, the fuel is oxidized by the metal oxide. Subsequently, the reduced oxygen carrier is reoxidized in the air reactor. The fuel reactor effluent consists only of CO_2 and H_2O, therefore a pure CO_2 stream, not diluted by N_2, is produced after steam condensation, which can be further utilized or sequestrated.

The selection of the oxygen carrier is considered as one of the most essential components of the CLC process. The feasibility of the process relies mainly on the oxygen carrier's ability to transfer oxygen from the air reactor to the fuel reactor. Furthermore, a successful oxygen carrier should have [1,5] high reactivity towards both the fuel and air, be stable during repeated oxidation/reduction cycles at high temperature and be environmentally benign and economically feasible. In addition it has to present mechanical resistance to the friction stress associated with high circulation of particles and low tendency to agglomeration, fragmentation and attrition. As a means to enhance the mechanical strength of the particles, to be used in a circulating bed, a binder can be added to the redox active phase.

Many oxygen carrier materials for CLC both without and with a support material have been investigated and reported in the literature. In general, unsupported materials tend to show fast degeneration or low reactivity, whereas supporting them on an inert carrier seems to increase the porosity and reactivity of the active materials [6]. NiO supported on $NiAl_2O_4$ is probably the best CLC oxygen carrier with the highest Oxygen Transfer Capacity and reactivity [7]. However, NiO is highly toxic, potential carcinogenic (it is classified as C1) and of high cost.

In an effort to replace NiO, a wide variety of single transition metal oxides, such as, CuO, CoO, MnO and Fe_2O_3, have, thus far, been tested as Oxygen Carriers for Chemical Looping Combustion (CLC). However, none of above single metal oxides completely meets the OC criteria for CLC application. CuO shows exothermic characteristics but low melting point and thus low resistance to sintering and high agglomeration [8]. CoO has satisfactory reactivity and oxygen transfer capacity but high cost [9]. Fe_2O_3 has low cost and environmental benignity but low oxygen transfer capacity and reactivity [10]. Also, MnO is another environmental friendly and low cost material which has low reactivity and tendency to react with support oxides [11–13].

Of the potential metal oxide candidates, iron (Fe) remains the most favorable due to its abundance, low cost and low toxicity. Considering this and in order to improve the reactivity of the Fe-based carriers, many researchers prepared and tested mixed metal oxides containing variable Fe-oxide content, to potentially resolve many of the shortcomings associated with conventional single metal oxides. The use of mixed oxide systems Mn/Fe, Ni/Fe, Co/Fe and Cu/Fe has been suggested [14–40] with promising results. In many cases synergetic effects that enhanced the performance of the oxides for CLC were attributed to the formation of different crystalline phases, such as spinels or perovskites.

The Mn–Fe mixed oxide system is the most widely studied thus far [15–24] since iron and manganese oxides have low cost, very favorable environmental and thermodynamic properties and could potentially be suitable for CLC applications. However, the materials exhibit low physical stability, and exhibit lower oxygen transfer capacity than Ni based materials [18]. It has been observed [20] that the addition of Mn oxides had a positive effect on the chemical stability of Fe_2O_3 during multiple CLC cycles. Many studies have been performed in order to examine the optimum Mn:Fe ratio as well as the effect of mixed compounds formation with the spinel or perovskite structure. It was found [23,24] that the optimum Mn:Fe ratio strongly depends on the process temperature. While

at process temperatures higher than 900 °C a Mn content up to 25–33% increases the fuel conversion by enhancing the CLOU effect (Chemical-Looping with Oxygen Uncoupling), Mn content higher than 50% has been proven advantageous at lower temperature ranges, 700–850 °C. Spinel phases are formed after the reduction step [24], which are further oxidized to hematite (Fe_2O_3)–bixbyite $(Mn_yFe_{1-y})_2O_3$ mixtures after the air oxidation step.

The Ni–Fe mixed oxide system and the formation of the $NiFe_2O_4$ spinel phase has been investigated in several previous works [25–29]. The addition of only 3% wt. nickel oxide particles in a bed of Fe-based is sufficient to give a very high CH_4 conversion [25]. NiO particles react with CH_4 forming CO and H_2, because metallic nickel catalyzes the methane reforming. Since iron oxide reacts fast with CO and H_2, it is suggested that a combination of both types of oxides may show synergy effects with an increased overall rate of reaction with respect to iron. It has been found [28] that the formation of Fe–Ni mixed spinel compounds had a negative effect on the combustion efficiency by reducing the catalytic effect of Ni addition.

$NiFe_2O_4$ as well as $CoFe_2O_4$ spinels, have been examined as oxygen carrier mostly for H_2 production either by solar driven water splitting, or by chemical looping reforming processes [27,28,30]. Redox cycling of $NiFe_2O_4$ oxygen carriers in TGA showed [27] that the single phase spinel structure demonstrates higher redox cycling behavior and better stability than standard NiO and Fe_2O_3, thus proving the feasibility of using the $NiFe_2O_4$ as an oxygen carrier in a reversible chemical looping process.

In CLC, the combined $CoFe_2O_4$ oxygen carrier was tested in TGA, with a high sulfur coal and found [31] to have the desired reaction superiority over its reference oxide CoO or Fe_2O_3.

Finally investigations of the Cu–Fe–O system [14–16,32–35] have shown that, at all tested Cu:Fe ratios, the spinel $CuFe_2O_4$ is formed, integrating Cu and Fe metals into one oxide matrix with superior characteristics over single metal oxides. It was concluded that the formation of the spinel contributes to improved reactivity and stability over monometallic Fe carriers, thus $CuFe_2O_4$ has a high potential to be used in CLC. The spinel with the formula $Cu_{0.95}Fe_{1.05}AlO_4$, tested by Lambert et al. [16,36] was found to have high oxygen transfer capacity, high oxidation rate, but a relatively low reduction rate compared to a reference NiO–$NiAl_2O_4$ formulation.

Several novel Fe-based mixed oxides with the spinel structure and the general formula $A_xA'_{x'}B_yB'_{y'}O_4$, such as $NiAlFeO_4$, $CuFeGaO_4$, $Cu_{0.5}Ni_{0.5}AlFeO_4$ and $Co_{0.5}Ni_{0.5}AlFeO_4$ have shown [37] high oxygen transfer capacity and redox rates in CLC. However, further research is required concerning their chemical and mechanical stability, before they can yet be readily used in CLC units.

A major challenge in CLC is that many promising Fe-based compositions, present reduced physical stability, low melting point and poor mechanical resistance after multiple redox cycles. To improve their stability, the addition of an inert carrier material been suggested [15,20,36,38,39]. It has been shown [20] that the support-type has a significant effect on both reduction–oxidation reaction rates and may result in much more stable operation. Supports based on Ceria, Zirconia, YSZ have been encountered as well as other types of binders, such as alumina, silica, titanium dioxide, kaolin or sepiolite. Spinel phases have also been tested, since it is generally accepted that they are very stable at high temperatures and do not react with hydrocarbons. Among the spinels investigated, nickel aluminate is commonly used as a binder with NiO, while $MgAl_2O_4$ proved promising as it increases sintering resistance and stability of copper oxide [40].

However, the use of a support involves an additional cost as a result of the introduction of a non-reactive metal since; the slower the oxidation and reduction reactions, the more the inventory of