Fuel 195 (2017) 38–48

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Titanium substituted manganese-ferrite as an oxygen carrier with permanent magnetic properties for chemical looping combustion of solid fuels

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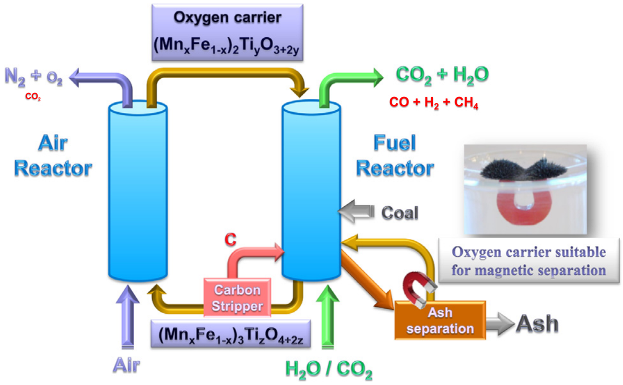
HIGHLIGHTS

- Particles with Mn/(Mn + Fe) = 0.55–0.87 show good performance for CLC with solids.
- $(Mn_xFe_{1-x})Ti_{0.15}O_z$ oxygen carriers can show permanent magnetic properties.
- The reactivity with fuel gases (CH_4, H_2 and CO) increases with the Mn content.
- The magnetic permeability increases as the Mn content decreases.
- Material with Mn/(Mn + Fe) = 0.55 is preferred considering its reactivity and magnetism.

GRAPHICAL ABSTRACT

The production method of MnFe mixed oxide particles has been developed in order to obtain permanent magnetic properties during redox cycles in CLC, which can be used for separation purposes of oxygen carrier particles in the purge stream of ash.



ARTICLE INFO

Article history:
Received 23 November 2016
Received in revised form 20 December 2016
Accepted 5 January 2017
Available online 18 January 2017

Keywords:
CO_2 capture
Chemical looping combustion
Oxygen carrier
Manganese oxide
Iron oxide
Magnetism

ABSTRACT

Mixed oxides of Mn-Fe have been identified as suitable materials for Chemical Looping Combustion (CLC) with solid fuels both via *in-situ* Gasification Chemical Looping Combustion (*i*G-CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) processes. These materials show the property of react with gaseous fuels as well as release oxygen under given conditions, while cheap metals are used. In addition, these materials can show magnetic properties that can be used for an easy separation from ash in CLC with solid fuels. Thus, losses of oxygen carrier material in the ash drain stream would be reduced. Different cations have been proposed for improving the magnetic properties of manganese ferrites, including Ti^{4+}. In this context, the present work accomplishes a screening of $(Mn_xFe_{1-x})_2O_3$ doped with 7 wt.% TiO_2, with x ranging from 0 to 1. The influence of Mn:Fe ratio on their physical and chemical properties was evaluated. In general, particles with high crushing strength values (>4 N) were obtained, and magnetic characteristics were highlighted when $x \leqslant 0.66$. The oxygen uncoupling capability depended on the Mn:Fe ratio and the oxidation conditions, i.e. temperature and oxygen partial pressure. Broader oxidation conditions to take advantage of the oxygen uncoupling capability were found for materials with low Mn content. On contrary, the reactivity with fuel gases (CH_4, H_2 and CO) increased with the Mn content. Thus, oxygen carriers with Mn/(Mn + Fe) molar ratio in the 0.5–0.9 interval showed interesting

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http://dx.doi.org/10.1016/j.fuel.2017.01.030
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properties at suitable temperatures for the *i*G-CLC and CLOU processes (i.e. 850–980 °C). The material with Mn/(Mn + Fe) = 0.55 was preferred considering a trade-off between reactivity and magnetic properties.

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1. Introduction

Nowadays, research involving the reduction of net CO_2 emissions to the atmosphere from combustion systems is still a challenge. Emerging combustion processes with intrinsic CO_2 capture, such as Chemical Looping Combustion (CLC), are of increasing interest since no energy or equipment is needed for gas separation as compared with the classic CO_2 capture systems (pre, post and oxyfuel combustion) [1]. Chemical Looping Combustion (CLC) implies the use of an oxygen carrier, generally a metal oxide, to transfer the oxygen from the air to the fuel. A CLC system basically consists of two interconnected fluidized beds, namely fuel and air reactors, with a particulate oxygen carrier continuously circulating between them [2]. In the fuel reactor, the fuel is combusted taken oxygen from the oxygen carrier, while the oxygen carrier is reoxidized with air in the air reactor. Thus, the direct contact between fuel and air is avoided and, the CO_2 capture is inherent to the CLC process.

Mainly, the use of solid fuels in CLC is being developed by two different approaches: *in-situ* Gasification Chemical Looping Combustion (*i*G-CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) [3]. In *i*G-CLC, the solid fuel is gasified by steam and/or carbon dioxide; then the generated gaseous products (mainly CO, H_2 and CH_4) react with the oxygen carrier to produce the combustion products (CO_2 and H_2O). When coal is considered the fuel, loss of oxygen carrier particles is expected in the drainage flow of ash. Thus, low cost materials such as ilmenite [4–6], iron ore [7–9], manganese ore [10] or waste materials [11] have been mostly evaluated for *i*G-CLC in pilot units up to 1 MW_{th}. In these cases, high CO_2 capture was achieved, but complete combustion was not reached [12]. In CLOU, the oxygen carrier is able to evolve gaseous oxygen in the fuel reactor, thus allowing the combustion of the solid fuel with O_2. The CLOU process was proposed by Mattisson et al. [13] to improve the combustion of solid fuels. Then, the proof of the concept was performed in a 1.5 kW CLOU unit by Abad et al. [14]. High CO_2 capture rates with complete combustion of different solid fuels (coal, lignite, biomass) was achieved by using a Cu-based oxygen carrier [14–16].

Alternatively to Cu-based materials, Mn-Fe mixed oxides have been identified as suitable materials for CLOU, while cheap and environmental friendly metals are used [17]. Bixbyite phase, $(Mn_xFe_{1-x})_2O_3$, must be formed during oxidation in order to show oxygen uncoupling capability during reduction to spinel phase, $(Mn_xFe_{1-x})_3O_4$ [18]. Thus, coal combustion was improved by taking advantage of the oxygen uncoupling capability of bixbyite when oxidation in the air reactor was optimized [19]. In addition, spinel phase $(Mn_xFe_{1-x})_3O_4$ can be reduced by fuel gases (e.g. H_2, CO, CH_4) to manganowüstite $(Mn_xFe_{1-x})O$, thus being active for *i*G-CLC [20–23].

The influence of the Mn:Fe ratio on the suitability of Mn-Fe mixed oxides for CLOU have been evaluated in the literature [21–25]. In general, oxygen carriers with Mn:Fe ratios higher than 0.6 show better fuel gas conversion and oxygen uncoupling capability at lower temperature (850 °C) than oxygen carriers with lower Mn:Fe ratios. But the potential for the oxidation to bixbyite improved as the Mn:Fe ratio was decreased [23]. i.e. they can be oxidized at higher temperatures, e.g. 950 °C, than materials with high Mn:Fe ratio.

Although manganese and iron can be considered as cheap materials, Mn-Fe mixed oxide materials must be sintered before used, thus increasing its prize compared to low-cost materials such as natural ores. Therefore, it would be very interesting the recovering of lost oxygen carrier particles with the ash. In this sense, Mn-Fe mixed oxides show magnetic properties in the spinel phase [26,27], which could be used for a magnetic separation from ash. Different cations have been proposed for improving the magnetic properties of manganese ferrites, e.g. by doping Mn-Fe mixed oxides with Ti^{4+} [28]. However, the magnetic properties of Mn-Fe mixed oxides in oxygen carriers for chemical looping applications have been not studied.

An oxygen carrier should accomplish the following characteristics: sufficient oxygen capacity, favorable thermodynamics regarding the fuel conversion to CO_2 and H_2O, high reactivity for reduction and oxidation reactions maintaining it during many successive redox cycles, resistance to attrition, negligible carbon deposition, good fluidization properties and environmental friendly characteristics [3]. In a previous work, Fe-Mn mixed oxides particles were obtained by mechanical mixing of Mn_3O_4 and Fe_2O_3 powders (Mn:Fe molar ratio of 0.77:0.33), which showed relatively high reactivity and crushing strength values (>1 N) [29]. Also, particles were prepared by doping with TiO_2 a material prepared by spray drying with Mn:Fe molar ratio of 0.66:0.34. These particles were successfully tested in a continuously operated CLC unit burning coal [19].

In this context, in the present work a screening of the performance of Mn-Fe-Ti based oxygen carriers, prepared with different Mn:Fe molar ratios and a fixed TiO_2 concentration, is performed. The characterization of the oxygen carriers has been based on the evaluation of their mechanical strength, the reduction and oxidation rates through TGA experiments at temperatures suitable for the *i*G-CLC and CLOU processes (i.e. 850–950 °C), and the determination of the magnetic susceptibility of the particles as a reference value to evaluate the applicability of the magnetic separation from ash.

2. Experimental

2.1. Oxygen carriers

The oxygen carrier particles were prepared using as raw materials Mn_3O_4 (Strem Chemical, Inc), Fe_2O_3 (Panreac, Prs), and TiO_2 (Panreac, Prs), all of them in powder. The mass fraction of TiO_2 was fixed to 7 wt.%, which was the fraction used in a previous tested material [19], but the Mn:Fe molar ratio was varied in a broad interval; see Table 1. To prepare the oxygen carriers, the reactants, in their respective mass fractions, were firstly ball-milled for 30 min and subsequently pelletized by pressure in a hydraulic press at 160 bar for 60 s, obtaining cylindrical pellets of about 1 cm in diameter and 3 cm in length. The pellets were further calcined at 1200 °C in a muffle furnace in air atmosphere during 2 h both, to increase the mechanical strength of the particles and to provide the material with permanent magnetic properties, considering results showed in [30]. In some cases, calcination at higher temperatures was required to provide magnetic properties. After calcination, materials with a general formula $Mn_xFe_{1-x}Ti_yO_z$

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