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Evaluation of $(Mn_xFe_{1-x})_2Ti_yO_z$ particles as oxygen carrier for Chemical Looping Combustion

María Abián, Alberto Abad*, María T. Izquierdo, Pilar Gayán, Luis F. de Diego, Francisco García-Labiano, Juan Adánez

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán, 4, Zaragoza, E-50018, Spain

Abstract

The present work accomplishes a screening of the performance of Mn-Fe-Ti based oxygen carriers, prepared with different Mn/(Mn+Fe) molar ratios in the general formula $(Mn_yFe_{1-y})Ti_{0.15}O_x$. The oxygen carriers were prepared by physical mixing followed by pelletizing under pressure, calcining, crushing and sieving in the 100-300 μm particle size interval. The characterization of the carriers is based on the evaluation of their crushing strength, magnetic properties and reduction and oxidation behavior through TGA experiments at temperatures suitable for the CLC process (i.e. 850-950 ºC). In addition, the main chemical structures of the Mn-Fe-Ti system were identified as a function of the Mn/(Mn+Fe) molar ratio. Oxygen uncoupling property was analyzed by reduction under a N_2 atmosphere and the capability to interact with fuel gases was analyzed by using CH_4, H_2 and CO.

Results indicate that the $(Mn_yFe_{1-y})Ti_{0.15}O_x$ oxygen carriers with Mn/(Mn+Fe) molar ratios of 0.55-0.87 have very promising properties for the CLC process with solid fuels.

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Keywords: CO_2 capture; CLC; CLOU; Manganese ferrites; Coal.

* Corresponding author. Tel.: +34-976-733-977; fax: +34-976-733-318.
E-mail address: abad@icb.csic.es

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1. Introduction

Chemical Looping Combustion (CLC) is an interesting CO_2 capture technology devoted to offer lower capture cost and efficiency penalty than the classic CO_2 capture systems [1]. The Chemical Looping Combustion technology implies the use of an oxygen carrier that circulates between a fuel and an air fluidized bed reactors. This way, the oxygen carrier transfers the oxygen from one to another reactor avoiding the direct contact between fuel and air [2]. There are two approaches for the use of the CLC technology with solid fuels: the *in-situ* Gasification Chemical Looping Combustion (*i*G-CLC) and the Chemical Looping with Oxygen Uncoupling (CLOU) [3]. Oxygen carriers with the capability to release gaseous oxygen in contact with the fuel are required for CLOU. In both *i*G-CLC and CLOU with coal, the generation of ash is, in general, inherent to the solid fuel combustion. Consequently, ash is drained to avoid its accumulation in the unit; and some oxygen carrier particles are also removed within the ash. The lost particles have to be replaced with new material. Thus, low-cost oxygen carriers have been considered for CLC. However, oxygen carriers for CLOU are generally synthetic materials, making them more expensive than minerals commonly used in *i*G-CLC. To reduce the cost of the oxygen carrier makeup, the oxygen carrier separation from ashes is required to be reintroduced in the system.

Mixed oxides of Mn-Fe have been identified as suitable materials for CLC having the property of release oxygen under given conditions, while cheap metals are used [4]. The Mn-Fe system has been considered in previous works (i.e. [5-8]), analyzing the influence of the Mn:Fe ratio on both, its chemical properties (reactivity and capability for releasing oxygen), and its mechanical strength. Main results from these studies indicate that the selection of the ideal Mn-Fe composition will depend on the specific operating conditions [8]. In general, for low temperatures (850ºC) oxygen carriers with high Mn:Fe ratios show better gas conversions and CLOU properties than oxygen carriers with low Mn:Fe ratios, and vice-versa for higher temperatures (900ºC and upper) [5].

In addition, the Mn-Fe mixed oxides can show magnetic properties that could be used for their easy separation from ash. In this sense, different cations such as Ti^{4+} have been proposed to improve the magnetic properties of manganese ferrites [9].

In this context, the present work accomplishes a screening of the performance of Mn-Fe-Ti based oxygen carriers, prepared with different Mn/(Mn+Fe) molar ratios. In particular, the crushing strength, magnetic properties and redox reactivity through TGA experiments are the main characteristics considered in this study.

The thermodynamic properties of the different $(Mn_yFe_{1-y})Ti_{0.15}O_x$ oxygen carrier, and consequently their performance in the CLC system, are conditioned by the specific structural composition of the particles. Figure 1 shows the theoretical stable phases predicted by thermodynamics (FToxid database from the FactSage software [10]) as function of different Mn/(Mn+Fe) molar ratios in the $(Mn_yFe_{1-y})Ti_{0.15}O_x$ system and temperature in an atmosphere with an O_2 partial pressure of 0.05 atm.

In the $(Mn_yFe_{1-y})Ti_{0.15}O_x$ system, low temperature regions are dominated by bixbyite (B) phases, while spinel (S) phase appear in the high temperature region. The temperature for the bixbyite (B) to spinel (S) transformation monotonically decreases as the Mn/(Mn+Fe) ratio increases. In the lower temperature regions, the hematite Fe_2O_3 and rutile TiO_2 phases dominate the regions with lower Mn content, whereas for higher Mn/(Mn+Fe) ratios bixbyte (B) and rutile (R) structures are the main phases present. At higher temperatures, rutile (R) and β-spinel (S) structures predominates in the regions with lower Mn content, whereas pyrophanite (P) and tetragonal spinel (S) gain importance as the Mn/(Mn+Fe) ratio increases. Between the regions dominated by bixbyite and spinel phases, there is a miscibility gap where both phases co-exist. These theoretical stable phases predicted by thermodynamics are compared to solid phases found after characterization of the oxygen carriers by XRD.

For the CLOU system, the oxygen release in the fuel reactor is typically produced from the transformation of bixbyite (B) to spinel (S) structure, and, as already indicated, in this system, the temperature for the bixbyite (B) to spinel (S) transformation decreases as the Mn content is increased. However, based on the phase diagram of Figure 1, when Ti is present in the mixture, oxygen uncoupling can be also produced from the transformation of spinel to pyrophanite structure. Pyrophanite is favoured at high Mn content.