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Research article

# Mn-based oxygen carriers prepared by impregnation for Chemical Looping Combustion with diverse fuels

T.R. Costa[a,b], P. Gayán[a], A. Abad[a,*], F. García-Labiano[a], L.F. de Diego[a], D.M.A. Melo[b], J. Adánez[a]

[a] Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castan 4, 50018 Zaragoza, Spain
[b] Chemical Institute (IQ-CCET), Federal University of Rio Grande do Norte, Natal, RN, Brazil

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ABSTRACT

Chemical Looping Combustion (CLC) is considered one of the low cost alternatives for $CO_2$ capture for fossil fuels combustion and to reach negative emissions through biomass CLC. The cornerstone of the CLC process is the oxygen carrier performance that represents the main additional cost with respect to the conventional combustion. Manganese-based oxygen carriers are subjected to a growing interest because they are low cost, not toxic and environmentally friendly. In this work five impregnated oxygen carriers, with manganese oxide $Mn_3O_4$ or $Mg_6MnO_8$ as their active phase and three commercial supports based on zirconia and synthetic calcium aluminate, were prepared. Their behaviour for CLC was examined by TGA, batch fluidized bed reactor, TPR, SEM-EDX and XRD. After a preliminary screening two carriers (Mn-ZrM and Mn-ZrSG) were subjected to multiple redox cycles by TGA and batch fluidized bed reactor. Both showed high solids conversion by TGA under the tested conditions, appropriated resistance to fracture, rate indexes relatively high, although Mn-ZrM showed agglomeration and deactivation during batch fluidized bed tests.

Reactivity in batch fluidized bed reactor of the Mn-ZrSG oxygen carrier with methane increases with temperature although suffered from significant deactivation. This was different to the results found during multiple redox cycles by TGA. There was not a clear reason for this decrease in the reactivity that likely could be due to the uncomplete oxidation in the batch fluidized bed reactor, although further investigations are needed. On the other hand, it presented high and constant reactivity with CO and $H_2$ in all the range of temperatures tested, being suitable for iG-CLC processes of coal or biomass and syngas combustion. Agglomeration problems were not found and the attrition losses were small. Calculated lifetime was around 11,000 h, much higher than any other Mn-based material developed or tested for CLC.

## 1. Introduction

Chemical Looping Combustion (CLC) is considered as a low cost process for $CO_2$ capture during combustion of gaseous and solid fuels due to its inherent $CO_2$ separation and its low energy penalty. Chemical Looping Combustion process is based on the transfer of the oxygen from the air to the fuel through a solid oxygen carrier, avoiding the direct contact between the fuel and the air. In CLC, as shown in Fig. 1, fuel and air are never mixed and this kind of combustion can be classified as an unmixed combustion [1]. In the first step (reaction 1), the fuel is oxidized to $CO_2$ and $H_2O$ by a metal oxide ($Me_xO_y$) that is reduced to $Me_xO_{y-1}$. The water generated in the process can be easily separated by condensation, thus obtaining a highly concentrated stream of $CO_2$, ready for transportation and storage [2]. The reduced metal oxide is further oxidized with air (reaction 2) in a second step and the regenerated material is ready for a new cycle.

$$(2n+m)\,Me_xO_y + C_nH_{2m} \rightarrow (2n+m)\,Me_xO_{y-1} + mH_2O + nCO_2 \quad (1)$$

$$Me_xO_{y-1} + O_2 \rightarrow 2\,Me_xO_y \quad (2)$$

CLC concept has been proposed to be carried out in different types or reactors and configurations. The more common configuration of the CLC system corresponds to two interconnected fluidized bed reactors, which are designated as: air reactor (AR) and fuel reactor (FR), with particles of metal oxide (oxygen carrier) circulating between the two reactors [2].

An overview of the CLC process applied to the combustion of gaseous and solid fuels can be found in a number of review publications [3–7]. In the last few years, significant efforts have been made in the area of oxygen carrier development [3,4,6]. Most of the oxygen carriers proposed in the literature as suitable for gas combustion ($CH_4$, natural gas, CO + $H_2$) are synthetic materials using as active metal oxides (CuO, $Fe_2O_3$, NiO and Mn oxides) and some mixed oxides with

* Corresponding author.
*E-mail address:* abad@icb.csic.es (A. Abad).

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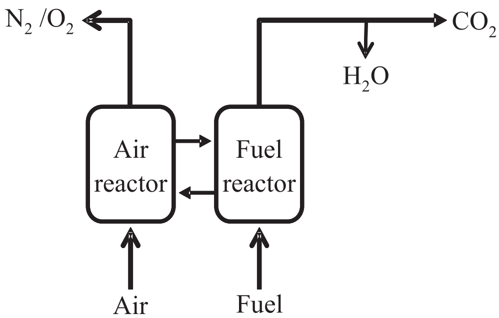


**Fig. 1.** Simplified diagram of the CLC system.

perovskite structure, containing Mn. Moreover, there are some studies showing the suitability of the use of minerals as iron and manganese ores, ilmenite or waste materials coming from steel industry and alumina production, although their performance is usually lower [6].

The cornerstone of CLC process is the performance of the oxygen carrier. This material must display a number of different characteristics in order to be suitable for CLC. Oxygen carriers needs to have sufficient oxygen transport capacity ($R_{OC}$), with high reactivity both for reduction and oxidation reactions and this must be maintained for a large number of redox cycles. Oxygen carriers need to have favourable thermodynamics regarding fuel conversion to $CO_2$ and $H_2O$. Moreover, negligible carbon deposition during reduction is needed to avoid C short-cutting to the air reactor, which reduces overall $CO_2$ capture efficiency. Good fluidization properties and no agglomeration in the reactors are fundamental for the smooth operation of interconnected fluidized bed reactors. Environmental and health issues must be considered to ensure the process meets future high standards of environmental performance.

Resistance to the attrition is a key point in order to reduce losses of elutriated fines and to reduce the oxygen carrier makeup costs when fluidized bed reactors are used. Thus, the main additional cost for CLC corresponds to the cost of the oxygen carrier replacement. The cost of the makeup stream of solids to replace the loss of fines will depend on: the lifetime of the oxygen carrier particles, the inventory in the CLC system and the cost of the oxygen carrier, which is mainly affected by the oxygen carrier reactivity, metal used and its content in the carrier. The oxygen carrier inventory depends mainly on the oxygen carrier reactivity; the redox pair used; the flow characteristics of gas and solids in the reactors, the solid circulation between reactors and the bed pressure drop [6]. Rate indexes can be used to extrapolate inventories, although give inaccurate values which only can be considered for initial estimations. However rate indexes can be used to compare the reactivity of different oxygen carriers. The rate index corresponds to the % of metal oxide mass that reacts per minute [8] and can be determined at a gas concentration corresponding to the mean value in the reactor.

$$\text{Rate index}\ (\%/\text{min}) = 60\cdot 100\ (\mathrm{d}\omega/\mathrm{d}t) \quad (3)$$

where ω is calculated by $\omega = m/m_{ox}$, $m_{ox}$ being the mass of the sample in the most oxidized state and $m$ the mass of the sample at any reacting time $t$.

Ni oxygen carriers suffer from environmental and health risks and Cu is a relatively expensive material and temperatures lower than 900 °C are recommended due to the low Tammann temperature of metallic copper, as well as in order to extend the lifetime of most promising materials impregnated on alumina [6]. On the contrary iron is considered a low cost and non-toxic material, although reactivity of Fe-based oxygen carriers is limited. Mn-based oxygen carriers are also cheap materials, non-toxic and environmentally friendly. Moreover, they have high melting point and oxygen transport capacity when compared with Fe-based oxygen carriers.

Mn-based oxygen carriers accomplish most basic requirements to be used as oxygen carrier [6] and when compared with iron carriers, it developed a similar or a superior activity, besides being inexpensive and non-toxic [9]. Another benefit is that some fuels have sulphur compounds in their composition, that react with the oxygen carrier forming sulphides in the CLC process, for example, materials that have in their base Ni and Co. However, manganese-based carriers, are thermodynamically stable in a CLC environment with fuels that have sulphur in their composition [6,10].

Several oxidation states may be involved in redox reactions of manganese. $MnO_2$, compound decompose in air at 500 °C, while the $Mn_2O_3$ is thermodynamically stable in air at temperatures below 900 °C [6,11,12]. Thus, the redox transformation among $Mn_3O_4$ to MnO is considered the most feasible for CLC [6,13]. The $Mn_3O_4$/MnO system is capable to convert completely $CH_4$ to $CO_2$ and $H_2O$ [10]. Despite the promising properties of manganese to be used as oxygen carrier, few materials based on Mn were tested in CLC, especially when compared to nickel, copper and iron.

Synthetic manganese-based oxygen carriers reported in the literature are combinations of active phase and support, where in most of them solid state reactions between Mn and the support occurred, decreasing the reactivity of these materials. Manganese-based carriers deposited/impregnated with alumina or silica, usually presented aluminates and silicates formation, respectively. The formation of these mixed oxides, reduces the reactivity of the material, presenting low fuel conversion [8,11,14–16]. Titanium oxide ($TiO_2$) was also used as a support for $Mn_3O_4$, showing low reactivity due to the formation of titanates during the sintering process of the material [15]. Some comprehensive screening studies [8,15–21] selected Mn-based oxygen carriers supported on $ZrO_2$ or $ZrO_2$ stabilized with MgO as suitable for CLC process.

One oxygen carrier selected in [8] containing 40% $Mn_3O_4$ and 60% MgO stabilized $ZrO_2$ was tested in a 300 W continuous CLC unit [9] at temperatures from 850 to 950 °C burning syngas and natural gas during 70 h with encouraging results. This carrier was best suited for syngas combustion reaching combustion efficiencies higher than 99%. For natural gas combustion efficiencies of 87.8% at 850 °C and 99% at 959 °C were found. Although crushing strength was 1.1 N, the attrition losses found were low, 0.038%/h, with a calculated lifetime of 2630 h. The reaction kinetics was determined for this carrier and reaction orders of 1 for reduction with $CH_4$ and 0.65 with $O_2$ were found. The activation energies were 119 kJ/mol and 19 kJ/mol for the reduction and the oxidation respectively [12].

Manganese ores have a great potential to be considered as oxygen carriers in CLC processes using solid fuels or syngas and its reactivity has been measured in different investigations. Depending of the origin of the ore the reactivity and the attrition behaviour show significant differences [22–28]. Mn-Fe mixed oxides depending on the composition and calcination conditions are capable of generate gaseous oxygen and also to use lattice oxygen for $CH_4$, CO and $H_2$ combustion [28–32]. Some investigations on Mn-Fe mixed oxides have been also carried out showing the capability of this kind of materials to burn fuels in CLC units [32–34]. Rydén et al. [33,34] used Fe-Mn and Mn-Fe-Ti [34] materials in a 300$W_{th}$ unit to burn methane. Good conversion of methane was found although the lifetime of the particles was extremely short. $(Mn_{0.77}Fe)_2O_3$ was investigated in a 500$W_{th}$ unit burning gaseous fuels and also different solid fuels [32] showing good reactivity for CO, $H_2$ and solid fuels with high lifetimes (6120 h).

The aim of this work is the development of impregnated Mn based oxygen carriers using different supports and their characterization for Chemical Looping Combustion. Mn-based oxygen carriers prepared by incipient wetness impregnation on $CaAl_2O_4$ and $ZrO_2$ of different sources were developed and examined for CLC by TGA and batch fluidized bed reactor testing. In order to select promising materials for CLC in continuous units, oxygen carriers were evaluated regarding the mechanical properties, reactivity with fuel gases and $O_2$ in order to select the more promising materials. Selected materials were further tested in a batch fluidized bed reactor during multiple redox cycles with fuel gases to know the fluidization behaviour, agglomeration behaviour