Evaluation of the redox capability of manganese-titanium mixed oxides for thermochemical energy storage and chemical looping processes

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Abstract

Manganese oxides are capable of releasing molecular oxygen and regenerate in air under determined conditions. This fact makes these materials interesting for applications in different areas, such as thermochemical energy storage processes, oxygen production by chemical looping air separation (CLAS) or CO₂ capture-oriented processes, namely chemical looping combustion (CLC) or chemical looping with oxygen uncoupling (CLOU).

In this work, the potential to release molecular oxygen and regenerate in air of different manganese-titanium mixed oxides with mass fractions of titanium from 0 to 50%, were evaluated in a TGA apparatus. Besides, the reactivity of the mixed oxide samples to the main fuel gases (CO, H₂ and CH₄) has been also evaluated. Consecutive redox cycles have been performed at different temperatures (850 and 940 °C) using nitrogen during reduction and air in oxidation. The oxygen transport capacity as well as the rate index
for oxygen uncoupling and gas-solid reactions have been determined and compared to
that found for other materials reported in literature. Moreover, solid phase identification
in the different mixed oxide samples by XRD has been addressed in order to determine
the oxygen release/regeneration mechanism. Results show a great potential of these
materials as low-cost and environmentally friendly oxygen carriers.

Keywords: thermochemical storage; air separation; chemical looping; manganese;
titanium; oxygen uncoupling

1. Introduction

The main contributor to CO₂ emissions to the atmosphere is the energy sector with an
important dependence on the fossil fuel resources [1]. To reach the goal set by the Paris
Agreement [2] significant changes should be addressed in the next future in the way
energy is produced. They include the enhancement of energy efficiency, the deployment
of low-carbon technologies (like solar, thermal or PV, and wind), the development of
carbon capture and storage (CCS) technologies and even removing CO₂ previously
emitted to the atmosphere. An important growth in the low-carbon technologies is
expected for the next decades supported by advances in the overcoming of the
intermittent nature of the renewable sources of energy, their main drawback [3]. This
can be realized by storing the energy via physical or chemical storage (thermochemical,
electromagnetic or electrochemical). On the other hand, CCS technologies have
potential to significantly reduce CO₂ emissions from the energy sector [4]. CCS
technologies produce concentrated CO₂ streams easy to transport and storage.
However, they are penalized by the energetic cost associated to the CO₂ separation steps
or oxygen production in the case of oxyfuel technologies [5]. Chemical looping combustion (CLC) technology has attracted attention because of its potential to reduce these costs [4]. CLC is based on the indirect combustion with solid oxygen carriers. CLC is highly flexible and it can be adapted to the so-called combined heat and power (CHP) or combined cooling heating and power (CCHP) processes [6]. However, depending on the thermochemical properties of the oxygen carriers, these materials can be used in different processes focused not only on energy generation with CO₂ capture [7], but also in air separation [8] or energy storage [9-11].

1.1. Thermochemical processes with oxygen carriers

In CLC, the oxygen needed in combustion is transferred from the air to the fuel by the oxygen carrier, which is normally a metal oxide. The metal oxide present in the oxygen carrier (MeₙOₙ) is reduced, yielding the oxygen available for the combustion of the fuel, see reaction (R1).

\[(2n + m/2)\text{Me}_x\text{O}_y + C_nH_m \rightarrow (2n + m/2)\text{Me}_x\text{O}_{y-1} + n\text{CO}_2 + (m/2)\text{H}_2\text{O}\]  
(R1)

Subsequently, the reduced oxygen carrier (Meₙ₋₁Oₚ) is regenerated with oxygen from air:

\[2\text{Me}_x\text{O}_{y-1} + O_2 \rightarrow 2\text{Me}_x\text{O}_y\]  
(R2)

Thus, there is not contact between fuel and air and penalization due to CO₂ separation from the rest of the exhaust gases is avoided. Moreover, the energy generated in the combustion is equivalent to that obtained in the conventional combustion. Since its development with energy production purposes, the most used oxygen carriers for the CLC process are oxides based on nickel, copper, iron and manganese [12]. The oxygen uncoupling capability of some of these metal oxides is interesting to separate oxygen from air in the so-called chemical looping air separation (CLAS) [13].
The CLAS process uses the fact that some metallic oxides are able to generate \( \text{O}_2 \) at high temperature, between 800 °C and 1200 °C, and then regenerate with air. The redox system should have suitable thermodynamic for the following chemical equilibrium:

\[
2Me_xO_y \leftrightarrow 2Me_{x-1}O_y + O_2 \tag{R3}
\]

This equilibrium is also of interest for the combustion of solid fuels because the conversion efficiency of the fuel is higher with materials showing oxygen uncoupling capability [14]. In this case, the process is named chemical looping with oxygen uncoupling (CLOU). In CLOU, the fuel is mainly burnt by the molecular oxygen released by the metal oxide in reaction (R3).

\[
C_nH_m + \left( n + \frac{m}{4} \right)O_2 \rightarrow nCO_2 + \left( m/2 \right)H_2O \tag{R4}
\]

The reduced oxygen carrier is again regenerated in air according to reaction (R2).

Three redox pairs have suitable thermochemical properties to be used in CLOU and CLAS, namely CuO/Cu2O, Mn2O3/Mn3O4, and Co3O4/CoO [15]. The proof of concept of the CLOU process was carried out with a copper-based oxygen carrier [16]. However, the production of these copper-based materials for CLOU process is costly and low-cost alternatives, such as manganese oxides, should be investigated. In addition, certain mixed oxides and perovskites, mostly based on manganese, showed improved thermochemical properties compared to the mono-metallic systems [17]. Moreover, the conditions at which these redox pairs operate (high temperature) and the nature of the process itself (air can act as both reactant and heat transfer fluid) make these materials also interesting for thermochemical energy storage coupled with electricity production from renewable sources, compensating for their intermittence and therefore enabling a continuous supply [10, 18].

1.2. Manganese-based oxygen carriers
Considering their oxygen uncoupling capability and independently of the final application considered the oxygen carriers must have special characteristics necessary to react in a reversible way with the oxygen at high temperature, so that they are able to release oxygen and recover it cyclically. The oxygen uncoupling capability of manganese oxides is based on the decomposition of Mn$_2$O$_3$ to Mn$_3$O$_4$; see reaction (R5).

\[ 6 \text{Mn}_2\text{O}_3 \leftrightarrow 4 \text{Mn}_3\text{O}_4 + \text{O}_2 \]  

(R5)

Therefore, Mn$_3$O$_4$ oxide should be regenerated to Mn$_2$O$_3$ in air by the inverse of the previous reaction. So far, the regeneration capability in air of monometallic Mn$_2$O$_3$-based materials for use in CLOU or CLAS is not usually observed [14]. The regeneration temperature should be lower than 800-850 ºC, which hinder the reactivity for the oxidation reaction [19]. Recently, an oxygen carrier prepared by manganese impregnation on zirconia showed the oxygen uncoupling capability at temperatures lower than 800 ºC [20]. Nevertheless, the redox system Mn$_3$O$_4$/MnO is the only proved for the fuel conversion in chemical looping units [14].

In order to take advantage of the oxygen uncoupling capability of manganese oxide, the most used practice has been the development of mixed oxides or perovskites [17]. Mixed oxides are based on mixtures of manganese with other metals without oxygen uncoupling capability to increase the regeneration temperature, e.g. iron, magnesium or silicon. These materials showed improved fuel conversion values than mono-metallic materials, with the exception of copper [14]. However, high excess of air was required to be properly regenerated, which could penalize the energetic efficiency of the process [21]. Perovskites are mainly based on CaMnO$_3$ with addition of some dopants as magnesium and/or titanium to improve the perovskite regeneration [22]. However, these materials showed low reactivity with fuel gases, and high excess of circulating solids
was required to achieve high fuel conversion due to their low oxygen transport capacity for oxygen uncoupling [23].

These kinds of materials based on mixed oxides including manganese and other metals have been also developed for CLAS and thermochemical energy storage [8]. Different studies point to iron oxides as the most effective doping material in order to improve the performance of the Mn₃O₄/Mn₃O₄ system for both CLAS [8] and thermal energy storage [24]. The addition of iron oxide allows faster oxidation rates [25], more stable cycle stability [25-27], lower thermal hysteresis [25] and higher energy storage density [28-30], although it could affect the mechanical strength. In order to improve attrition of the particles, CeO₂, ZrO₂ and TiO₂ have been also used as dopants [31].

1.3. The Mn-Ti-O redox system

On the contrary of manganese mixed oxides with iron, magnesium or silicon, the MnTi-mixed oxide system has been little studied for use as an oxygen carrier. When oxygen carriers based on manganese oxide supported on TiO₂ have been evaluated for the CLC process [32], they were discarded because of its low reactivity with CH₄ due to the formation of manganese titanates during the thermal treatment stage.

In a study by Rydén et al. [33] manganese based ilmenite analogue pyrophanite (MnTiO₃) was examined as potential oxygen carrier for the CLOU process. Pyrophanite (MnTiO₃) showed very little gas release of O₂ and presented very poor reactivity with methane. Therefore, it was considered as unsuitable to be used as oxygen carrier.

In other work, Abián et al. [34] studied materials based on mixtures of Mn and Fe oxides, in different proportions -(MnₓFe₁₋ₓ)₂O₃, with x between 0 and 1- and tried to optimize their magnetic properties by titanium oxide addition (7 wt%). In the case of x = 1 (absence of iron oxide) the material obtained showed an ability to release oxygen
and regenerate in air higher than that of pure manganese oxide in the same reaction conditions. This capability can be explained by the Mn-Ti-O diagram; see Figure 1 [35, 36]. The diagram shows the solid phase solutions that were found as a function of the molar fraction of titanium and the temperature.

![Figure 1. Phase diagram of the Mn-Ti-O system as function of the Ti/(Ti+Mn) molar ratio and temperature in air ($p_{O_2} = 0.21$ atm) [36].](image)

| H (Hausmannite, Mn$^{2+}$Mn$^{3+}$O$_4$) | S (Spinel, Mn$_3$O$_4$) |
| B (Bixbyite, α-Mn$_2$O$_3$) | P (Pyrophanite MnTiO$_3$) |
| R (Rutile TiO$_2$) |

Considering the Ti content, there can be established two regions in the diagram. One corresponds to titanium molar fractions lower than the titanium fraction in pyrophanite (Ti/(Ti+Mn) $< 0.5$). In the phase regions 8-10, located in the low temperature zone, manganese is found in bixbyite solid solution (Mn$_3$O$_3$) while in the high temperature
regions 1-4, the predominant phase is spinel or hausmannite solid solution (Mn$_3$O$_4$).

Under these conditions, the increasing presence of titanium increases the temperature for the transformation of Mn$_2$O$_3$ to Mn$_3$O$_4$ following reaction (R5). For pure manganese, this reaction happens above 890 °C in air. For Ti/(Ti+Mn) < 0.14 aprox., Mn$_2$O$_3$ is progressively decomposed to Mn$_3$O$_4$ as temperature increases in regions 6 and 7. In air, the complete conversion of Mn$_2$O$_3$ into Mn$_3$O$_4$ is found at 995 °C for Ti/(Ti+Mn) in the 0.02-0.08 interval and at 1020 °C for Ti/(Ti+Mn) in the 0.1-0.14 interval. For Ti/(Ti+Mn) in the 0.14-0.5 interval, the transformation of Mn$_2$O$_3$ to Mn$_3$O$_4$ also happens at 1020 °C in air. However, pyrophanite appears from titanium molar fraction about 0.12 and temperatures above 890 °C (interphase of regions 9 and 10) following reaction (R6), i.e. Mn$_2$O$_3$ and TiO$_2$ can decompose to pyrophanite releasing O$_2$. The latter transformation is the only existing for titanium molar fractions higher than 0.5, i.e when there is an excess of TiO$_2$ in the solid solution.

$$2\text{Mn}_2\text{O}_3 + 4\text{TiO}_2 \leftrightarrow 4\text{MnTiO}_3 + \text{O}_2 \quad \text{(R6)}$$

From these results, it may be deduced that the titanium fraction in these Mn-Ti mixed oxides seems to affect to the interesting oxygen uncoupling ability of releasing molecular oxygen and regenerating in air and should be investigated further. In general, oxygen is released when Mn$_2$O$_3$ decompose into Mn$_3$O$_4$, but reduction of Mn$^{3+}$ to Mn$^{2+}$ can be also promoted by the formation of pyrophanite (MnTiO$_3$). These transformations should also be considered to select a suitable temperature for the regeneration of Mn$_2$O$_3$ by air.

1.4. Objective

The objective of the present study was to further investigate mixed oxides combining manganese oxide and titanium oxide and analyze the influence of the percentage of TiO$_2$ added to pure Mn$_3$O$_4$ on the ability of the combined oxide to release pure oxygen
and regenerate in air. Samples with different TiO$_2$ percentages will be prepared and
their main properties determined. Moreover, the reactivity in N$_2$/air atmospheres will be
characterized in a TGA apparatus as well as their capability to react with some of the
main fuel gases (CO, H$_2$ and CH$_4$).

2. Experimental

2.1 Preparation of the materials

Nine different materials were prepared by mechanical mixing of precursor powders:
Mn$_3$O$_4$ (Micromax ®, ELKEM) and TiO$_2$ (Panreac Prs). Table 1 shows a summary of
the materials prepared and their main physical properties. The different proportions of
the raw materials were mixed in a ball mill for 30 minutes. Then, the mixtures were
pelletized by pressure in a hydraulic press at 165 bar during 60 seconds. Cylindrical
pellets were so obtained of about 1 cm in diameter and 3 cm in length. These pellets
were calcined in a muffle in air at 1030 °C during 2 hours in order to achieve a material
with high enough mechanical strength. After calcination, the pellets were crushed and
sieved to the desired size (100-300 µm).

The crushing strength of the particles was measured using a Shimpo FGN-5X crushing
strength apparatus. This technique determines the force needed to fracture a particle.
The value reported for sample was the average value of 20 measurements. The main
phases of the Mn-Ti mixed oxides were identified by X-ray diffraction (XRD). The
XRD analysis was performed using a Bruker D8 Advance X-ray powder diffractometer
equipped with an X-ray source with a Cu anode working at 40 kV and 40 mA and an
energy-dispersive one dimensional detector. In particular, the diffraction pattern was
obtained with a scanning step of 0.019º over the 2θ range of 10–80º, and the assignation and quantification of crystalline phases was performed through the use of the DIFFRAC.EVA and TOPAS software, on base of Joint Committee on Powder Diffraction Standards.
**Table 1.** Main properties of the Mn-Ti mixed oxide samples after calcination in air at 1030 ºC for 2 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn$_3$O$_4$ (wt.%)</th>
<th>TiO$_2$ (wt.%)</th>
<th>Ti/(Ti + Mn)$^a$</th>
<th>Crushing strength (N)</th>
<th>XRD main phases (wt. %)</th>
<th>Mn$_3$O$_3$</th>
<th>Mn$_3$O$_4$</th>
<th>MnTiO$_3$</th>
<th>Mn$_2$TiO$_4$</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnTi 0</td>
<td>100</td>
<td>0</td>
<td>0.00</td>
<td>3.4</td>
<td>69.0</td>
<td>31.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnTi 7</td>
<td>93</td>
<td>7</td>
<td>0.07</td>
<td>5.5</td>
<td>18.0</td>
<td>65.2</td>
<td>5.5</td>
<td>11.3</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>MnTi 10</td>
<td>90</td>
<td>10</td>
<td>0.10</td>
<td>4.9</td>
<td>77.0</td>
<td>17.6</td>
<td>4.8</td>
<td>-</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>MnTi 15</td>
<td>85</td>
<td>15</td>
<td>0.14</td>
<td>4.6</td>
<td>59.7</td>
<td>20.0</td>
<td>19.4</td>
<td>-</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>MnTi 20</td>
<td>80</td>
<td>20</td>
<td>0.19</td>
<td>3.7</td>
<td>64.2</td>
<td>11.5</td>
<td>23.6</td>
<td>-</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>MnTi 25</td>
<td>75</td>
<td>25</td>
<td>0.24</td>
<td>3.3</td>
<td>43.2</td>
<td>13.6</td>
<td>39.4</td>
<td>-</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>MnTi 33</td>
<td>67</td>
<td>33</td>
<td>0.32</td>
<td>3.5</td>
<td>25.4</td>
<td>14.5</td>
<td>55.3</td>
<td>-</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>MnTi 43</td>
<td>57</td>
<td>43</td>
<td>0.42</td>
<td>4.4</td>
<td>3.8</td>
<td>2.5</td>
<td>89.3</td>
<td>-</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>MnTi 50</td>
<td>50</td>
<td>50</td>
<td>0.49</td>
<td>3.7</td>
<td>0.6</td>
<td>1.9</td>
<td>91.9</td>
<td>-</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Molar ratio
2.2 Thermogravimetric analyser (TGA) and procedure

The experiments performed in this study were carried out in a thermogravimetric analyser (TGA CI Electronics). The detailed description of the TGA and procedure can be found elsewhere [37] and therefore only a brief description is given here. The oxygen carrier mass and gas flow used in the TGA experiments were chosen to avoid limitations in the external film mass-transfer and/or inter particle diffusion. Moreover, the crucible used to hold the sample during the experiment was a wire mesh platinum basket especially designed to minimize problems of gas diffusion in the crucible.

For each test, around 50 mg of oxygen carrier particles were loaded and heated up to the desired temperature (850 or 940 °C) in an air atmosphere. The reacting temperatures were chosen in order to oxidize the material in regions with presence of Mn2O3 or Mn3O4/MnTiO3, respectively; see Figure 1. A total gas flow of 25 L/h (STP) was used in all cases. After stabilization, the oxygen carrier particles were exposed to five successive reduction-oxidation cycles with duration of 30 min each. To analyse the oxygen uncoupling properties of the Mn-Ti mixed oxides, decomposition-regeneration cycles were performed alternating highly-pure N2 (<2 ppm O2) and air at the corresponding temperature. Specific experiments with 80 mg of sample were done in order to obtain enough amounts to determine solid phases formed after reduction in nitrogen or oxidation in air.

To analyse the reactivity of the samples prepared with the main combustion gases (CO, H2 and CH4) experiments were also performed with 50 mg of material at both 850 and 940 °C. The concentration of the reducing gases used was: 15% H2, 15% CO + 20% CO2 and 15% CH4 + 20% H2O, respectively. In this case, the reduction to MnO was
promoted and XRD analyses were also used to identify the solid phases existing in the reacted sample.

2.3 Analysis of the TGA results

The oxygen transport capacity for a specific redox transformation, \( R_{OC} \), is defined as the mass fraction of the mixed oxide sample that can be transferred as oxygen:

\[
R_{OC} = \frac{m_o - m_r}{m_{oxid}}
\]  

(1)

where \( m_o \) is the initial mass of the sample in the oxidized state, \( m_r \) the mass of the sample in the reduced state and \( m_{oxid} \) the mass of the fully oxidized sample.

Once the value of oxygen transport capacity is known, the conversion for reduction \( (X_{red}) \) and oxidation \( (X_{ox}) \) of each of the mixed oxide samples could be calculated as:

\[
X_{red} = \frac{m_o - m}{R_{OCmoxid}}
\]  

(2)

\[
X_{ox} = \frac{m - m_r}{R_{OCmoxid}}
\]  

(3)

The oxygen transport capacity for the oxygen uncoupling will be denoted as \( R^u_{OC} \).

Considering the presence of TiO\(_2\) and the phase diagram in Figure 1, reactions (R5) and (R6) may participate in the oxygen uncoupling mechanism.

Reduction of Mn\(_3\)O\(_4\) can only proceed in the presence of a reducing agent. Thus, the oxygen transport capacity related to this reduction will be denoted as \( R^g_{OC} \). Thus, the total oxygen transport capacity \( (R^t_{OC}) \) of the mixed oxide sample will be defined as

\[
R^t_{OC} = R^u_{OC} + R^g_{OC},
\]

in a similar way to previous works with Mn-based mixed oxides [23, 36].

Another parameter to be calculated from TGA results is the rate of oxygen transference per unit of mass. For oxygen uncoupling it is calculated as follows:

\[
r_{O_2} = R^u_{OC} \cdot \frac{dX_{ou}}{dt}
\]  

(4)
The reaction rate for oxygen uncoupling was determined in N₂, and 21 vol% O₂ was considered for the oxidation. The rate index for the oxygen uncoupling reaction was defined as follows:

\[
Rate \text{ index } \left( \%_{\text{min}} \right) = 60 \cdot 100 \cdot r_{O_2}
\] (5)

Finally, the reactivity with the different fuel gases was analyzed by the normalized rate index [38] defined as:

\[
Rate \text{ index } \left( \%_{\text{min}} \right) = 60 \cdot 100 \cdot R_{DC}^i \cdot \left( \frac{dX_i}{dt} \right)_{\text{norm}, 15\% \text{gas}}
\] (6)

3. Results and Discussion

3.1. Mn-Ti-O redox system for chemical looping

The phase diagram for the Mn-Ti-O system at \( p_{O_2} = 0.21 \text{ atm} \) as a function of the temperature and the Ti/(Ti+Mn) ratio was shown in Figure 1. As it can be seen in Table 1, the Ti/(Ti+Mn) molar ratios of interest in this work vary between 0 and 0.49. Thus, the coexistence of Mn₂O₃ and MnTiO₃ could be promoted, and the material could be partially oxidized to Mn₂O₃ at a higher temperature, which is beneficial for CLOU [39].

The phase diagram in Figure 1 can explain the phase composition of the different manganese-titanium mixed oxides samples after calcination shown in Table 1. To have a visual reference of the samples composition, one symbol for each sample was included in Figure 1 considering the composition in the corresponding interphase lines due to most of the samples were mainly composed by three phases. As it was mentioned, the samples were calcined in air at 1030 °C for 2 h. The stable phases at this temperature depends on the Ti/(Ti+Mn) atomic ratio. Thus, for ratios lower than 0.1 the stable phase is a solid solution of TiO₂ in Mn₃O₄, either in the spinel or hausmannite form. The Mn₃O₄ found in calcined samples (Table 1) can be explained by the
equilibrium at 1030 ºC. However, after calcination at 1030 ºC, the cooling step began, also in air atmosphere, at an estimated cooling rate (not controlled) of 2-5 ºC /min. During this process, Mn$_2$O$_3$ could be produced at a temperature between 890 and 1020 ºC, with the fraction of Mn$_3$O$_4$ oxidized to Mn$_2$O$_3$ being a function of the kinetics of reverse of reaction (R5). In addition, Mn$_2$O$_3$ can be also formed by oxidation of pyrophanite (MnTiO$_3$) at a lower temperature by reverse of reaction (R6).

From XRD results in Table 1 it can be observed that there is high amount of Mn$_3$O$_4$ found in the sample MnTi$_7$, which happens when spinel can be formed in region 6 for Ti/(Mn+Ti) $\approx$ 0.07. In addition, some MnTiO$_3$ was found in MnTi$_7$ and MnTi$_{10}$ samples. This fact was expected for MnTi$_{10}$, where part of the Mn$_3$O$_4$ was converted to MnTiO$_3$ by reaction with TiO$_2$. This would not be the case for MnTi$_7$, but the formation of MnTiO$_3$ could be due to inhomogeneity in the solid sample, with local compositions allowing the formation of this phase.

When the Ti/(Mn+Ti) ratio was increased over 0.1 the formation of MnTiO$_3$ was promoted at the expense of Mn$_2$O$_3$. Following the results shown in Table 1 it can be said that almost all of TiO$_2$ in the sample was consumed to form MnTiO$_3$, since almost no free TiO$_2$ was identified in the calcines samples. However, during the cooling, MnTiO$_3$ did not significantly oxidize back to Mn$_2$O$_3$ and TiO$_2$, which would be expected below 890 ºC during the cooling process. Moreover, some Mn$_3$O$_4$ remained still in the solid samples which decreased with the Ti/(Mn+Ti) ratio increase. This behaviour corresponds to the existing phase between 890 and 1020 ºC.

According to the phase diagram, the manganese-titanium oxide mixtures would be able to generate O$_2$ via two routes. Mn$_2$O$_3$ may decompose to Mn$_3$O$_4$ following reaction (R5). As it was described for CLOU, pure Mn$_3$O$_4$ is formed above 890 ºC in air. But the
transition temperature increases as TiO_2 was added in the 0-0.1 interval for the
Ti/(Mn+Ti) ratio; see Figure 1. For higher ratios, the transition temperature between
Mn_2O_3 and Mn_3O_4 was about 1020 °C. Table 2 shows the theoretical oxygen transport
capacity for this reaction, here named as \( R_{O_{OC}}^{ou-I} \). For this calculation it was assumed that
all manganese was as Mn_2O_3 in the oxidized form.

For materials with Ti/(Mn+Ti) ratios higher than ~0.1, oxygen can be also released
following reaction (R6). The theoretical oxygen transport capacity for this reaction is
shown in Table 2 as \( R_{O_{OC}}^{ou-II} \). In this case, it was assumed all titanium was in the
pyrophanite phase (MnTiO_3). Eventually, the \( R_{O_{OC}}^{ou-III} \) parameter was included to
consider the decomposition of Mn_2O_3 to Mn_3O_4 of the remaining manganese after
MnTiO_3 formation in samples with Ti/(Mn+Ti) ratios higher than 0.1. The total oxygen
uncoupling capacity, as defined by equation (1), was calculated as \( R_{O_{OC}}^{ou-IV} = R_{O_{OC}}^{ou-II} +
R_{O_{OC}}^{ou-III} \). \( R_{O_{OC}}^{ou-IV} \) would be achieved when the material was oxidized at a temperature
lower than 890 °C. If material was oxidized at a temperature between 890 °C and 1020
°C, Mn_2O_3/MnTiO_3 mixtures are achieved and the maximum oxygen transport capacity
would be described by the \( R_{O_{OC}}^{ou-III} \).

From the CLOU or thermochemical energy storage point of view, the oxidation at a
lower temperature than 890 °C would represent an increase in the oxygen transport
capacity (\( R_{O_{OC}}^{ou-IV} \)) compared to that of manganese oxide without interaction with
titanium oxide, described by the parameter \( R_{O_{OC}}^{ou-I} \). Oxidizing at a higher temperature
supposes the decrease of the oxygen transport capacity (\( R_{O_{OC}}^{ou-III} \)), but it is still better
than the case of pure manganese. It must be remembered that pure manganese oxide has
not oxygen uncoupling capability under this condition because is not feasible the
oxidation of Mn_3O_4 to Mn_2O_3.
In the presence of a reducing gas, e.g. H₂, CO or CH₄, a further reduction of Mn₃O₄ to Mn²⁺ species is allowed. According to Yankin et al. [35], MnO is formed for Ti/(Mn+Ti) ratios lower than 0.3, while MnTiO₃ is promoted for higher ratios. In any case, the fraction of oxygen in the solid is the same after the reduction, and the oxygen transport capacity only depends on the phase achieved during the oxidation stage. Table 2 shows the value of the total oxygen transport capacity considering complete oxidation to Mn₂O₃ ($R_{OC}^{f-I}$), partial oxidation to Mn₃O₄ ($R_{OC}^{f-II}$), or the oxidation to a Mn₂O₃/MnTiO₃ mixture for Ti/(Mn+Ti) ratios higher than 0.1 ($R_{OC}^{f-III}$).

Table 2. Total oxygen transport capacity ($R_{OC}^{f}$) and those for the oxygen uncoupling capability ($R_{OC}^{ou}$) of Mn-Ti mixed oxides, considering the following redox pairs: $R_{OC}^{ou-1}$: Mn₂O₃/Mn₃O₄ without restrictions; $R_{OC}^{ou-II}$: Mn₂O₃/MnTiO₃; $R_{OC}^{ou-III}$: Mn₂O₃/Mn₃O₄ with MnTiO₃ formation; $R_{OC}^{ou-IV}$: Mn₂O₃/Mn₃O₄+MnTiO₃; $R_{OC}^{f-I}$: Mn₂O₃/MnO or Mn₂O₃/MnTiO₃; $R_{OC}^{f-II}$: Mn₃O₄/MnO; $R_{OC}^{f-III}$: Mn₂O₃+MnTiO₃/MnO+MnTiO₃. Grey cells are redox pairs considered in this work according to Figure 1.

<table>
<thead>
<tr>
<th></th>
<th>$R_{OC}^{ou-1}$</th>
<th>$R_{OC}^{ou-II}$</th>
<th>$R_{OC}^{ou-III}$</th>
<th>$R_{OC}^{ou-IV}$</th>
<th>$R_{OC}^{f-I}$</th>
<th>$R_{OC}^{f-II}$</th>
<th>$R_{OC}^{f-III}$</th>
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<tr>
<td>MnTi 0</td>
<td>3.38</td>
<td>0.00</td>
<td>3.38</td>
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<td>6.76</td>
<td>10.13</td>
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<td>MnTi 7</td>
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<td>3.60</td>
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<td>6.30</td>
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</tr>
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<td>6.10</td>
<td>8.18</td>
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<td>2.40</td>
<td>3.86</td>
<td>8.66</td>
<td>5.77</td>
<td>7.20</td>
</tr>
<tr>
<td>MnTi 20</td>
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<td>2.07</td>
<td>4.02</td>
<td>8.16</td>
<td>5.44</td>
<td>6.21</td>
</tr>
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<td>1.74</td>
<td>4.18</td>
<td>7.67</td>
<td>5.11</td>
<td>5.23</td>
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<td>4.44</td>
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<td>1.64</td>
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<tr>
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<td>5.00</td>
<td>5.15</td>
<td>3.44</td>
<td>0.23</td>
</tr>
</tbody>
</table>

3.2. Evaluation of the oxygen uncoupling capability

3.2.1. Oxygen transport capacity
First of all, the oxygen transport capacity for oxygen uncoupling of the manganese-titanium mixed oxides prepared in this work was calculated by TGA tests. Figure 2 shows an example of a typical experiment where it is observed the stable behaviour of the sample through the successive cycles. As mentioned before, the oxygen carrier particles experienced five reduction-oxidation cycles, both at 850 °C and 940 °C. According to Figure 1, oxidation to Mn$_2$O$_3$ is feasible at 850 °C, but oxidation to Mn$_3$O$_4$/Mn$_2$O$_3$ or Mn$_2$O$_3$/MnTiO$_3$ mixtures must be considered at 940 °C.

![Graph](image_url)

**Figure 2.** Reduction and oxidation cycles in TGA at 850°C for the sample with 15 wt% TiO$_2$. Reduction was performed using nitrogen and oxidation in air.

Table 3 and Figure 3 show the values obtained for $R_{O_C}^{uu}$ in experiments in TGA at 850°C and 940 °C. As it can be seen in Figure 3, the oxygen transport capacity for the oxygen uncoupling process ($R_{O_C}^{uu}$) presents a maximum value of 1.4 % in the 0.14-0.19 Ti/(Mn+Ti) interval (corresponding to 15-20 % TiO$_2$) at both temperatures tested. At 850 °C, the maximum transport capacity corresponds to the sample with 20 % TiO$_2$. 

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while at 940 ºC, the sample with 15 % TiO2 presents the maximum value. One of the facts that should be highlighted in Figure 3 is that the addition of TiO2 seems to favour the regeneration of Mn2O3 in conditions where the pure Mn3O4 has not been observed to be oxidized (temperatures higher than 850 ºC). Nevertheless, the conversion values shown in Table 3 are lower than the unity due to the reaction was not completed during the reduction period; see Figure 2.

Table 3. Oxygen uncoupling capability for the Mn-Ti mixed oxide samples corresponding to the fifth cycle in TGA at 850 and 940 ºC. The reference value of $R_{OC}^{ref}$ to calculate the conversion values were taken from Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>850 ºC</th>
<th>940 ºC</th>
<th>850 ºC</th>
<th>940 ºC</th>
<th>850 ºC</th>
<th>940 ºC</th>
<th>850 ºC</th>
<th>940 ºC</th>
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<tr>
<td></td>
<td>$R_{OC}$</td>
<td>$R_{OC}^{ref}$</td>
<td>$x_{red}^{ou}$</td>
<td>$R_{OC}$</td>
<td>$R_{OC}^{ref}$</td>
<td>$x_{red}^{ou}$</td>
<td>$R_{OC}^{t}$</td>
<td>$R_{OC}^{ref}$</td>
</tr>
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<td>0.00</td>
<td>0.0</td>
<td>3.4</td>
<td>0.00</td>
<td>7.5</td>
<td>10.1</td>
</tr>
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<td>3.2</td>
<td>0.13</td>
<td>0.7</td>
<td>3.2</td>
<td>0.22</td>
<td>6.9</td>
<td>9.4</td>
</tr>
<tr>
<td>MnTi_10</td>
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<td>3.0</td>
<td>0.23</td>
<td>1.1</td>
<td>3.0</td>
<td>0.36</td>
<td>6.0</td>
<td>9.2</td>
</tr>
<tr>
<td>MnTi_15</td>
<td>1.3</td>
<td>3.9</td>
<td>0.34</td>
<td>1.4</td>
<td>2.4</td>
<td>0.58</td>
<td>5.6</td>
<td>8.7</td>
</tr>
<tr>
<td>MnTi_20</td>
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<td>4.0</td>
<td>0.35</td>
<td>1.2</td>
<td>2.1</td>
<td>0.58</td>
<td>4.3</td>
<td>8.2</td>
</tr>
<tr>
<td>MnTi_25</td>
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<td>1.7</td>
<td>0.63</td>
<td>4.3</td>
<td>7.7</td>
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<td>4.4</td>
<td>0.20</td>
<td>0.9</td>
<td>1.2</td>
<td>0.74</td>
<td>3.3</td>
<td>6.9</td>
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<td>0.18</td>
<td>3.3</td>
<td>5.9</td>
</tr>
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<td>MnTi_50</td>
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<td>0.00</td>
<td>0.0</td>
<td>0.1</td>
<td>0.00</td>
<td>1.0</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Figure 3. Oxygen uncoupling capability, $R_{OC}^{ou}$, as a function of Ti/(Mn+Ti) ratio in the mixed manganese-titanium oxide (results corresponding to the fifth cycle in TGA at 940°C and 850 °C).

Taking into account the reference values of the theoretical oxygen transport capacity as a function of the reacting temperature and TiO$_2$ fraction, the maximum in the oxygen transport capacity observed in Figure 3 was not initially expected and was investigated in more detail. For materials with Ti/(Mn+Ti) ratios lower than 0.1, the oxygen uncoupling capability is expected to happen mainly by decomposition of Mn$_2$O$_3$ into Mn$_3$O$_4$ ($R_{OC}^{ou-1}$). In this case, the oxygen uncoupling capability is quite lower than the theoretical prediction. This fact may be due to the partial conversion of either Mn$_3$O$_4$ oxidation or Mn$_2$O$_3$ reduction under these conditions.

For materials with a higher ratio, it is expected to happen from the reaction of Mn$_2$O$_3$ and TiO$_2$ to form Mn$_3$O$_4$ and MnTiO$_3$ at 850 °C ($R_{OC}^{ou-IV}$); but at 940 °C titanium is in the form of MnTiO$_3$ which inertizes a fraction of manganese, and the contribution for
oxygen uncoupling is due to the Mn$_2$O$_3$/Mn$_3$O$_4$ with the remaining manganese
($R_{OC}^{III}$). Therefore, the theoretical values at 940 °C are lower than at 850 °C. However,
similar values of $R_{OC}^{III}$ were experimentally observed at both reacting temperatures, and
they were similar to theoretical values at 940 °C. This fact suggests that the active redox
pair is similar in both cases, being the oxidized solid a mixture of Mn$_2$O$_3$ and MnTiO$_3$
considering the phase diagram at 940 °C; see Figure 1. At this point, it can be speculated
that the presence of titanium inertizes a fraction of manganese in the MnTiO$_3$ form,
even at 850 °C where the formation of a mixture of Mn$_2$O$_3$ and TiO$_2$ would be feasible.
New dedicated experiments were performed at TGA in order to better characterize the
redox processes taking place at both temperatures. First, samples were reduced for 30
min in N$_2$ and then quickly cooled down in N$_2$ atmosphere. After cooling, the solid
phases in the sample were identified and quantified by XRD. In another set of
experiments, samples were also reduced for 30 min in N$_2$, then oxidized for 30 min in
air and cooled down. Thus solid phases formed during oxidation were also characterized
by XRD.
Figure 4 shows the results obtained after reduction and after re-oxidation of the different
mixed oxide samples at both 850 and 940 °C. It can be corroborated that the manganese
moles that formed MnTiO$_3$ during calcination remained in that solid phase during the
successive reduction-oxidation cycles and therefore the oxygen release can be
completely associated to reaction (R5). In this figure, the percentage of manganese
moles that are found as Mn$_2$O$_3$, Mn$_3$O$_4$ or MnTiO$_3$ are represented for different
Ti/(Mn+Ti) ratios after the reduction and oxidation stage and for the two temperatures.
Results at 850°C indicate that not all the Mn$_2$O$_3$ in the sample is reduced to Mn$_3$O$_4$. However, oxidation in air seems to be favoured, since most of the manganese moles appear as Mn$_2$O$_3$. This behaviour was observed for all TiO$_2$ contents, but it would be only expected for Ti/(Mn+Ti) ratios lower than 0.1, considering the phase diagram in Figure 1. For higher ratios, the disaggregation of Mn and Ti would be expected to form a mixture of Mn$_2$O$_3$ and TiO$_2$. However, experimental results showed that pyrophanite (MnTiO$_3$) was formed, but manganese in pyrophanite was not oxidized to Mn$_2$O$_3$ by reverse of reaction (R6). Results at 940°C seem to indicate that Mn$_2$O$_3$ reduction to Mn$_3$O$_4$ is favoured at this temperature. For all the TiO$_2$ percentages analysed the only phase found is Mn$_3$O$_4$ during reduction. However, oxidation is not as favoured since

Figure 4. Percentage of Mn mol as Mn$_2$O$_3$, Mn$_3$O$_4$ or MnTiO$_3$ quantified by XRD of samples after reduction and oxidation at 850 and 940 °C.
only 44% Mn₂O₃ (at the most) is found in the oxidized samples. In addition, samples with high TiO₂ content (43 and 50%) were mainly composed by MnTiO₃ and barely reacted in the redox cycles; see Figure 4.

As a conclusion it can be said that Mn₂O₃/Mn₃O₄ was the only active redox pair for oxygen uncoupling reaction at both temperatures and any TiO₂ content. The conversion achieved depended on the TiO₂ content and reacting temperature. The fraction of pyrophanite increased with TiO₂ content, and it was inert for the oxygen uncoupling reaction. The combination of these factors justified the maximum in the oxygen transport capacity observed at Ti/(Mn+Ti) ratios of 0.15-0.2, which were included in the preferred embodiments of a patent by authors [40].

3.2.2. Oxygen transference rate

Figure 5 presents the normalized rate indexes for the manganese-titanium samples as a function of the Ti/(Mn+Ti) ratio. At 940 ºC, rate indexes for the oxygen uncoupling larger than 0.3 %/min were obtained for samples with 0.1-0.32 Ti/(Mn+Ti), i.e. TiO₂ content between 10 and 33 %. A maximum value of 0.56 %/min was achieved with Ti/(Mn+Ti) = 0.2. However, the rate index values for the oxidation are much lower, which is related to the low conversion of Mn₃O₄ to Mn₃O₄ presented in Figure 4. In the case of the experiments at 850 ºC, the oxygen carrier oxidation rate is increased by 2-3 times, but the reactivity for oxygen uncoupling was clearly decreased. Thus, the rate index for oxidation and oxygen uncoupling achieved similar values. It is clear from these results that the reduction/oxidation conditions applied in a future continuous CLC use of these new materials should be carefully optimized for an adequate exploitation of their CLOU properties because of the required thermal integration between fuel and air reactors. However, the optimum temperature during oxygen uncoupling and oxidation
stages for thermochemical energy storage can be easily selected since these stages are independent of each other.

**Figure 5.** Normalized rate index as a function of Ti/(Mn+Ti) in the reduction with nitrogen and oxidation in air for the mixed manganese-titanium oxide (results corresponding to the fifth cycle in TGA at both 940ºC and 850 ºC).

The rate index values for the MnTi materials are lower than those reported for Cu-based. Cu-based materials present high oxygen transfer rates, oscillating between 3.7 %/min [41] and 6 %/min [42, 43]. However, mixed oxides based on manganese are being developed as a low cost alternative to the costly Cu-based oxygen carriers existing for CLOU although Mn-based materials may not outperform the behaviour of the Cu-based ones [14]. Thus, oxygen transfer rates of the manganese-titanium mixed oxides developed in this work are compared to those reported in literature for other Mn-based oxygen carriers, mainly based on MnFe mixed oxides [34, 44]. In order to compare the mixed oxides tested in the present work with other Mn-based oxygen...
carriers used in the CLOU process, Table 4 compares the maximum normalized rate indexes in reduction with nitrogen and oxidation in air found for different type of materials. In MnFe-mixed oxides, Pérez-Vega et al. [44] reported optimum values for the normalized rate index in reduction with nitrogen and oxidation in air at 870 °C (see Table 4). These rate indexes can be compared to the maximum values of rate index obtained in the present work at 850 °C, corresponding to the samples with Ti/(Mn+Ti) 0.14 (15 % TiO₂). The rate indexes for the MnFe material at 870 °C were higher than those corresponding to MnTi_15. Moreover, the oxygen transport capacity for the MnFe-mixed oxide is 3.0 %, higher than the maximum oxygen transport capacity of the manganese-titanium samples (see Figure 3).

The rate index at 940 °C corresponding to the samples with Ti/(Mn+Ti) equal to 0.19 (20 % TiO₂) can be compared with results available for a MnFe-mixed oxide doped with Ti [34]. The normalized rate indexes determined for this material, identified as Mn55FeTi7, in the reduction with nitrogen and oxidation with air at 950 °C were included in Table 4. In this case, the rate index for the reduction in nitrogen of the MnTi_20 samples is almost six times the value reported for Mn55FeTi7 although the rate index for the oxidation is lower than the corresponding to the manganese-iron sample. In this case, the oxygen transport capacity of both materials is similar.

Considering all the results above, it can be said that the manganese-titanium samples developed in the present work improve the regeneration in air of the manganese oxide alone. Moreover, these samples may present oxygen uncoupling capabilities comparable to those reported in literature for other Mn-based oxygen carriers and these properties can be further optimized in order to consider the use of the manganese-titanium mixed oxides in processes requiring oxygen release and uptake.
3.3. Evaluation of the reaction with fuel gases

To complete the study of the reactivity of the manganese-titanium mixed oxides developed in this work, their reactivity with the main combustion gases, i.e. H₂, CO and CH₄ (reduction stage) and O₂ (oxidation stage) was also analysed in the TGA apparatus. Manganese oxides, both Mn₂O₃ or Mn₃O₄, may also be reduced by reaction with a fuel gas present in the fuel reactor atmosphere (e.g. CO, H₂ or CH₄) as indicated in reactions (R7) to (R12).

\[
\begin{align*}
3 \text{Mn}_2\text{O}_3 + H_2 & \rightarrow 2 \text{Mn}_3\text{O}_4 + H_2O \quad \text{(R7)} \\
3 \text{Mn}_2\text{O}_3 + CO & \rightarrow 2 \text{Mn}_3\text{O}_4 + CO_2 \quad \text{(R8)} \\
12 \text{Mn}_2\text{O}_3 + CH_4 & \rightarrow 8 \text{Mn}_3\text{O}_4 + CO_2 + 2 H_2O \quad \text{(R9)} \\
\text{Mn}_3\text{O}_4 + H_2 & \rightarrow 3 \text{MnO} + H_2O \quad \text{(R10)} \\
\text{Mn}_3\text{O}_4 + CO & \rightarrow 3 \text{MnO} + CO_2 \quad \text{(R11)} \\
4 \text{Mn}_3\text{O}_4 + CH_4 & \rightarrow 12 \text{MnO} + CO_2 + 2 H_2O \quad \text{(R12)}
\end{align*}
\]

3.3.1. Oxygen transport capacity

Figure 6 and Table 3 present the values of the total oxygen transport capacity \(R_{OC}^t\) in the reaction with hydrogen as a function of the TiO₂ percentage in the mixed oxide at both 850 and 940 °C. On one hand, no big differences were observed between the values estimated for both temperatures. On the other hand, the values of \(R_{OC}^t\) decrease as the content of TiO₂ in the mixed oxide increase. Figure 6 also presents the reference values of the total oxygen transport capacity for the samples considering the phase diagram in Figure 1 for oxidized conditions, as well as reduction to MnO or MnTiO₃.
Figure 6. Total oxygen transport capacity ($R_{OC}^t$) as a function of the Ti/(Mn+Ti) ratio in the mixed manganese-titanium oxide (results corresponding to the fifth cycle in TGA with reduction in H₂ in TGA at 940 ºC).

Mn₂O₃ was considered the oxidized form at 850 ºC, which corresponds to the $R_{OC}^t$ values in Table 2. At 940 ºC, Mn₃O₄ is the oxidized form of manganese for Ti/(Mn+Ti) ratios ≤ 0.1, which corresponds to $R_{OC}^{t-II}$ values in Table 2. For higher ratios, a mixture of Mn₂O₃ and MnTiO₃ would be expected after oxidation, corresponding to $R_{OC}^{t-III}$ values in Table 2. The reference values calculated for 940 ºC agree with those found experimentally at both 850 and 940 ºC, except in some specific cases, namely materials with high TiO₂ content at 850 ºC.

A further study based on XRD quantification of crystalline solid phases found in the samples after one semi-cycle with hydrogen reduction and one cycle H₂ reduction-air oxidation; see Table 5. After reduction, up to four solid phases can be found, namely Mn₃O₄, MnO, MnTiO₃ and Mn₂TiO₄. This fact suggests that some Mn₃O₄ could not be
reduced to MnO, especially for Ti/(Mn+Ti) ratios ≤ 0.1. However, the oxygen transport
capacity was increased compared to theoretical calculations at this temperature because
some Mn$_2$O$_3$ was formed during the oxidation stage. This fact was not considered for
the theoretical calculations at 940 °C at low Ti/(Ti+Mn) ratios, although some Mn$_2$O$_3$
formation is expected from the phase diagram in Figure 1. In general, mostly Mn$_3$O$_4$
can be found after oxidation. In addition, most of manganese initially present in the
form of MnTiO$_3$ at the beginning of the cycles does not take part in the redox reactions
taking place as it has been previously observed in the experiments in N$_2$-air. MnTiO$_3$
becomes the main compound for high Ti contents.
Table 4. Normalized rate index obtained for other Mn-based synthetic oxygen carriers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CLOU</th>
<th>CLC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Mn₇₇Fe[L₄] [44]</td>
<td>870 °C: N₂-air</td>
<td>0.30 1.10</td>
</tr>
<tr>
<td></td>
<td>950 °C: H₂/CO/CH₄-air</td>
<td>10.4 3.3 2.5 8.4</td>
</tr>
<tr>
<td>Mn₅₅Fe₇Ti [34]</td>
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<td>0.10 0.45</td>
</tr>
<tr>
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<td>850 °C</td>
<td>0.06 0.06</td>
</tr>
<tr>
<td>MnTi₂₀ [This work]</td>
<td>940 °C</td>
<td>0.56 0.02</td>
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Table 5. Weight percentages of the solids phases identified by XRD at 940 °C after reduction with H₂ and reduction with H₂+oxidation in air.

<table>
<thead>
<tr>
<th>TiO₂ (%)</th>
<th>Mn₂O₃</th>
<th>Mn₃O₄</th>
<th>MnO</th>
<th>MnTiO₃</th>
<th>Mn₂TiO₄</th>
<th>TiO₂</th>
<th>Mn₂O₃</th>
<th>Mn₃O₄</th>
<th>MnO</th>
<th>MnTiO₃</th>
<th>Mn₂TiO₄</th>
<th>TiO₂</th>
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<tbody>
<tr>
<td></td>
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<td>MnTiO₃</td>
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<td>48.4</td>
<td>51.6</td>
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<td>33</td>
<td>25.2</td>
<td>61.2</td>
<td>13.6</td>
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<td>2.6</td>
<td>97.4</td>
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<tr>
<td>50</td>
<td>3.3</td>
<td>90.5</td>
<td>6.2</td>
<td></td>
<td></td>
<td></td>
<td>2.6</td>
<td>97.4</td>
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</table>
3.3.2. Oxygen transference rate

The evolution of the values of normalized rate indexes at the different temperatures for the Ti/(Mn+Ti) ratios is shown in Figure 7(A) at 850 ºC and Figure 7(B) at 940 ºC. The highest values were always obtained at 940 ºC with all the gases. At 850 ºC, all of the samples presented a very low reactivity to methane. The sample MnTi_50, mostly constituted by pyrophanite (MnTiO\textsubscript{3}) was not reactive with any of the gases tested at any of the temperatures considered. This may explain the decrease in the rate index observed when the TiO\textsubscript{2} content was higher than 25 %, since larger pyrophanite fractions are present in the samples with a higher TiO\textsubscript{2} content.

![Graph](image)

**Figure 7.** Normalized rate index for H\textsubscript{2}, CO, CH\textsubscript{4} and oxygen at (A) 850 and (B) 940 ºC corresponding to the fifth cycle in TGA as a function of the Ti/(Mn+Ti) molar ratio.

The rate indexes obtained for H\textsubscript{2}, CO, CH\textsubscript{4} and oxygen for the samples with the highest oxygen uncoupling capability were included in Table 4 and compared to those found for other Mn-based synthetic materials. If results for MnTi_20 at 940 ºC are compared to those corresponding to MnFe materials at 950 ºC it can be seen that the MnTi_20 presents higher rate indexes in the reaction with hydrogen and with O\textsubscript{2}. The main differences in reactivity are found in the values for CO and CH\textsubscript{4} of the MnTi_20
sample, which are similar to those found for MnFe and higher than those found for the Ti-doped MnFe material. This result again confirms the potential of the manganese-titanium mixed oxides as oxygen carriers not only for oxygen uncoupling processes but also in their application to other chemical looping systems.

3.4. Discussion

The addition of TiO₂ in a range 15-20% wt. to the system Mn₂O₃/Mn₃O₄ has demonstrated to be beneficial for the regeneration in air of Mn₃O₄ at temperatures in which the pure oxide is not able to reoxidize. This fact opens the possibility of using the materials for chemical looping processes (CLOU or CLAS) and thermochemical storage. Compared to other materials based on copper or cobalt proposed for CLOU-CLAS or thermochemical storage, the manganese-titanium mixed oxides identified in our work present some advantages, mainly related to the cost of the material, as well as health and safety issues. In this respect, these materials are not expected to be as costly as copper or cobalt oxides but similar to those corresponding to the Mn-Fe system [24]. As an example, the cost of Co₃O₄ is estimated in 250 €/kg while the cost of Mn₃O₄ and TiO₂ is estimated as 12 and 2.5 €/kg, respectively [30].

For CLOU or CLAS applications, the oxygen transport capacity and reactivity (referred to rate index) of Mn-Ti materials under the conditions studied are similar, or even higher in some cases, than those showed by Mn-Fe mixed oxides, as it was discussed in Table 4. As it was also mentioned in the introduction section, Mn-Fe materials have been proposed as dopants of the Mn₂O₃/Mn₃O₄ system to overcome the limitation of Mn₃O₄ regeneration in air. The addition of Fe₂O₃ facilitated the oxidation in air and increased the stability of the cycles, but several problems regarding sintering and/or
disintegration of the particles after long cycling have been reported [11, 45]. Therefore, Mn-Ti deserves to be further explored as an alternative system to Mn-Fe.

Regarding the application of Mn-Ti materials for thermochemical storage, concentrated solar energy (CSP) can be used to reduce an oxygen carrier with oxygen uncoupling capability. Recently, some authors proposed a CSP system based on metal oxide particles as thermochemical energy storage material [46, 47]. The concept combines extraction of sensible and thermochemical energy and it consists of a working heat exchanger and solar receiver with two storage tanks in between. The metal oxide particles are reduced in the solar receiver and then conveyed to a high-temperature storage tank. Then, the energy discharge is performed in a separate reactor by oxidation of the particles with air. After that, the material is transferred to a low-temperature storage tank and then sent back to the solar tower. Several designs for the solar receivers have been proposed, including fluidized beds or falling particles which allow high temperatures in the solar receptor (1000°C or higher) [48]. For the discharging step, moving bed reactors have been already tested using Mn-Fe oxygen carriers [46].

Especially in the case of thermochemical storage, the reaction enthalpies and the temperature window for the redox transformation of the materials are key parameters to be considered, since this can define the type of thermochemical storage to be applied [24]. The application as storage material in concentrated solar plants (CSP) would limit the redox temperature to 850 °C for oxidation stage, while temperatures of 950 °C or higher could be used in the solar receiver. Considering these conditions, the thermochemical storage capability of Mn-Ti and Mn-Fe materials are shown in Table 6. Calculations were done using data previously derived from HSC and FactSage software [39]. For the material with stoichiometry (Mn0.66Fe0.34)3O4, the total thermochemical
storage capability is 354 kJ/kg, of which 76.1% is provided by chemical transformation from \((\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4\), to \((\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3\), being the rest sensible heat. However, it was difficult to take advantage of the entire thermochemical energy because only 50% of \((\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4\) may be oxidized to \((\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3\) in a real case [21]. Thus, the effective oxygen transport capacity is one half of the theoretical, and the thermochemical storage capability is decreased to 223 kJ/kg, being 61.4 % due to chemical energy. For pure \(\text{Mn}_3\text{O}_4\), the theoretical oxygen transport capacity is comparable to Mn-Fe, but lower chemical energy could be stored. However, the value of 262 kJ/kg is higher than that of 223 kJ/kg in a real case with Mn-Fe. However, addition of 20 % \(\text{TiO}_2\) was required in this work to take advantage of the oxygen uncoupling property with \(\text{Mn}_3\text{O}_4\). In addition, about 50% of \(\text{Mn}_3\text{O}_4\) could be oxidized to \(\text{Mn}_2\text{O}_3\), which reduced the effective oxygen transport capacity to \(R_{OC} = 1.4\%\). As a consequence, the capability of thermochemical storage is decreased to 161 kJ/kg, being 45.1% chemical energy. This fact demands an increase in the effective \(\text{Mn}_3\text{O}_4\) being oxidized to \(\text{Mn}_2\text{O}_3\).

Table 6. Conversion to the oxidized form, oxygen transport capacity and capability of thermochemical storage for Mn-Ti and Mn-Fe materials. Oxidation: 850 °C; reduction: 950 °C.

<table>
<thead>
<tr>
<th></th>
<th>(\text{Mn}_3\text{O}_4) (theoretical)</th>
<th>(\text{Mn}_3\text{O}_4+20%\text{TiO}_2) (this work)</th>
<th>((\text{Mn}<em>{0.66}\text{Fe}</em>{0.34})_3\text{O}_4) (theoretical)</th>
<th>((\text{Mn}<em>{0.66}\text{Fe}</em>{0.34})_2\text{O}_3) (practical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X_{ox})</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>(R_{OC}) (%)</td>
<td>3.4</td>
<td>1.4</td>
<td>3.4</td>
<td>1.7</td>
</tr>
<tr>
<td>Thermochemical energy storage (kJ/kg)</td>
<td>262</td>
<td>161</td>
<td>354</td>
<td>223</td>
</tr>
</tbody>
</table>
Chemical energy storage (kJ/kg)  
176  73  269  137  

Fraction of chemical energy stored (%)  
67.4  45.1  76.1  61.4  

Alternatively, H₂ from renewable sources can be used as a reducing agent if the oxygen carrier has not oxygen uncoupling capability. Thus, the oxygen carrier can be considered a material to store energy. The following oxidation can be performed by air to produce heat or H₂O to produce H₂ when required [49]. In addition, the thermochemical energy can also be stored in solids of a fluidized bed boiler when a fuel is burnt, e.g. natural gas, coal or biomass. This concept has been proposed in order to operate the boiler in a continuous regime, regardless of the energy demand variation during a time period [50]. In these cases, the Mn-Ti material studied in this work shows a total oxygen transport capacity of $R_{OC} = 7\%$ allowing a complete conversion of the fuel to CO₂ and H₂O while Mn₂O₃ and Mn₃O₄ is reduced to MnO. Similar effective oxygen transport capability was found for Mn-Fe material, but a complete reduction to Mn₃O₄₆₆Fe₀₃₄O does not allow the complete conversion of fuel to CO₂ and H₂O [39]. The reduction should be limited to a value about 60%, which reduces the effective oxygen transport capacity of Mn-Fe to $R_{OC} = 6\%$.

It should be mentioned that the preparation method for Mn-Ti materials should be optimized in further research and this can influence their reactivity. Further studies with the mixed oxides identified in the present work should be also accomplished in order to determine their behavior regarding mechanical properties under several redox cycles. In order to assess the use of Mn-Ti materials, further testing under reacting conditions such as solid fuel combustion should be considered. That will allow estimating the combustion efficiencies to be reached as well as the integrity of the material under
reacting conditions and therefore determine its lifetime in a CLC unit. However, the results already obtained seem promising.

4. Conclusions

In this work, the redox capability of manganese-titanium mixed oxides with Ti/(Mn+Ti) ratios between 0.1-0.49 was analysed. Samples were prepared by mechanical mixing of TiO₂ and Mn₃O₄ powders, pelletized and calcined at 1030 ºC during 2 h. The highest oxygen uncoupling capability in manganese-titanium oxide samples was 1.44 %. A rate index in the reduction with nitrogen of 0.56 %/min was found at 940 ºC for the sample with 0.19 Ti/(Mn+Ti) (20 wt.% TiO₂), which is higher than those previously reported for Mn-based materials under the same conditions. XRD analysis to reduced and oxidized samples during oxygen uncoupling confirmed that part of the original manganese forms pyrophanite (MnTiO₃) that, opposite to what was expected, did not participate in the oxygen uncoupling redox process. Thus, the oxygen release was mainly due to Mn₂O₃ reduction to Mn₃O₄. However, it seems that the presence of MnTiO₃ favoured the oxidation from Mn₃O₄ to Mn₂O₃ in conditions when the pure Mn₃O₄ did not oxidize. This characteristic makes these materials potential candidates to be used in the CLOU process or for thermochemical energy storage. Reducing and oxidation conditions should be carefully optimized in order to exploit the oxygen uncoupling capability of these materials and further study is required.
Acknowledgments

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