Evaluation of Mn-Fe mixed oxide doped with TiO₂ for the combustion with CO₂ capture by Chemical Looping *assisted by* Oxygen Uncoupling

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Abstract

Bimetallic manganese-iron materials have been identified as suitable oxygen carriers for Chemical Looping Combustion (CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) processes. These materials allow the combustion of a fuel with inherent CO₂ capture according to two parallel mechanisms: reaction with lattice oxygen and oxygen uncoupling. This work is focused on the evaluation of the reactivity and physicochemical characterization of oxygen carrier particles consisting of a manganese-iron mixed oxide with manganese to iron molar ratio of 66:34 and doped with titanium (7 wt% TiO₂) with the objective of determining suitable conditions to be used in CLC and CLOU processes. Particles were prepared by spray drying and the sintering procedure was optimized in order to achieve particles with high reactivity and mechanical strength. In addition, suitable magnetic properties were also sought in order to allow oxygen carrier recover and reuse in a chemical looping unit burning solid fuels. Optimum operating conditions for the fuel combustion and regeneration stages were determined in order to promote the oxygen uncoupling mechanism. Thus, temperature during the fuel combustion must be as high as possible to enhance the oxygen transference; but conditions for oxygen carrier regeneration

by air must be carefully selected in order to take advantage of the oxygen uncoupling capability of this material. An oxidizing temperature interval of 1123–1173 K maximized the regeneration, while an air excess higher than 20 % would be recommended in order to guarantee oxygen uncoupling capability.

Keywords: CO₂ capture; Chemical Looping Combustion; Oxygen uncoupling; Manganese; Iron; Oxygen carrier.

1. Introduction

Chemical Looping Combustion (CLC) is a combustion technology with inherent CO₂ capture and low energetic [1] and economical penalties [2]. CLC concept is based on the transfer of oxygen from the air to the fuel by using a solid oxygen carrier, which is continuously circulating between two interconnected fluidized bed reactors, namely the fuel and air reactors [3]. In this way, the contact between the fuel and air is prevented during all combustion process. Fuel oxidation to CO₂ and H₂O takes place inside the fuel reactor by means of the oxygen transferred by the oxygen carrier. As result, a highly concentrated CO₂ stream can be obtained after steam condensation. Afterwards, the spent oxygen carrier is regenerated in the air reactor being oxidized with air.

CLC of coal has been mainly developed via *in-situ* Gasification Chemical Looping Combustion (*iG*-CLC) [4], where steam and/or recycled CO₂ are supplied inside the fuel reactor as gasifying and fluidizing agent. Conversion of the gasification products to CO₂ and H₂O subsequently takes place by means of gas-solid reactions with the oxygen carrier. Low-cost oxygen carriers based on iron or manganese ores have widely been tested in *iG*-CLC facilities [4], being ilmenite [5], iron ores [6,7], manganese ores [8], and CaSO₄ from limestone [9] the most relevant ones. Usually, complete combustion of coal in the *iG*-CLC

process is not achieved; this fact would entail an energy penalty owing to the requirement for including a post-combustion step; e.g., an oxygen polishing unit [10]. This issue is more relevant when a fuel with high volatile content is used, such as biomass [11]. Therefore, the combustion efficiency was mostly in the 70-80 % interval when biomass was used in CLC units at Chalmers University of Technology [12], Southeast University [13], Darmstadt University of Technology [14], VTT [15], or CSIC [16].

The combustion efficiency may be improved by using some technological improvements, such as the gas-solid contact enhancement, implementing a secondary fuel reactor, recirculating unconverted compounds, feeding the fuel into the carbon stripper, [17] or employing a distributor for the volatile matter [10]. Some of these solutions have been tested in experimental CLC units. Thus, the combustion efficiency was improved by 20 % by promoting the gas-solid contact [18], or even by 90 % by using a secondary fuel reactor [19,20]. However, complete combustion has still not been achieved.

Alternatively, the use of oxygen carrier materials with the capability to release gaseous oxygen in the fuel reactor has the potential to achieve complete combustion of solid fuels [4] in the so-called Chemical Looping with Oxygen Uncoupling (CLOU) process [21]. Thus, complete combustion of coal has been obtained with Cu-based [22] and Cu-Mn mixed oxide materials [23]. In addition, both Cu- [24] and CuMn-based [25] materials also showed complete combustion of biomass, unlike the use of metal oxides without oxygen uncoupling capability [11].

Alternatively to Cu-containing materials, the system composed by Mn-Fe mixed oxide has been proposed as a cheaper oxygen carrier [26]. The oxygen uncoupling capability of Mn-Fe mixed oxide is based on the spontaneous release of molecular oxygen when the temperature is increased [27], or even when the partial pressure of oxygen is decreased, as it happens in the fuel reactor [28]. The most oxidized state corresponds to bixbyite

($\text{Mn}_x\text{Fe}_{1-x}$)₂O₃ phase, which has oxygen uncoupling capability. The variation of the oxygen concentration at equilibrium conditions with the reacting temperature depends on the Mn:Fe molar ratio [29]. As the oxygen concentration decreases below the equilibrium value, spinel ($\text{Mn}_x\text{Fe}_{1-x}$)₃O₄ phase is formed through oxygen uncoupling mechanism with an oxygen transport capacity of $R_{OC,\max}^{ou} = 0.034$; see reaction (R1).

At extremely low O₂ concentration, mangano-wüstite ($\text{Mn}_x\text{Fe}_{1-x}$)O phase can be formed. This transformation is facilitated by the presence of a reducing agent such as H₂, CO or CH₄ [30-32], see reactions (R2)-(R4), which implies an oxygen transport capacity of $R_{OC,\max}^g = 0.067$ [28].

Oxidation from mangano-wüstite to spinel is relatively fast [30]; see reaction (R5). On the contrary, oxidation of spinel to bixbyite, i.e., the reverse of reaction (R1), could be restricted by kinetic and/or thermodynamic limitations [29].

Therefore, the global capability of Mn-Fe mixed oxides to transfer oxygen includes both oxygen uncoupling (CLOU mode) and common reaction of gas with lattice oxygen in the solid (CLC mode). Considering that the amount of oxygen transferred by gas-solid reaction could be more relevant than those released *via* oxygen uncoupling, as it was for the case of Mn-Ca perovskites [33], the global process has been named as Chemical Looping *assisted by* Oxygen Uncoupling (CLaOU) [28]. This process is in contrast with the merely CLOU, for example with highly reactive Cu-based materials, where the main mechanism transferring oxygen could be the oxygen uncoupling [34].

Magnetic properties of spinel phase in the bimetallic Mn-Fe mixed oxide could be exploited for the oxygen carrier recovery from the ash purge stream [35,36]. It is expected that the purge stream of ash also includes oxygen carrier particles that could be re-used in the CLC unit. The concentration of oxygen carrier in the purge stream would depend on different parameters, such as the solid fuel ash content, the fly ash fraction and ash removal rate [37]. From an economic point of view, the recovery of oxygen carrier particles from the purge ash stream is a key factor to consider the use of synthetic materials. In this way, an oxygen carrier exhibiting magnetic properties would allow to recover the oxygen carrier from the ash purging stream in the CLC system and to reuse it, with the consequent cost reduction due to the lower material make-up requirement.

Most of the studies carried out on the use of Mn-Fe mixed oxide as oxygen carrier have been focused on the characteristics of oxygen releasing capability for fuel conversion with synthetic materials [27,29,38,39]. The Mn:Fe ratio is a key parameter to obtain particles with a relevant oxygen uncoupling capability [26]. The most innovative Mn-Fe mixed oxides materials include materials doped with Ca, Mg, Si [40] or Ti [36], materials based on geopolimers [41], materials synthesized under inert or reducing atmospheres [42] and manganese-modified ilmenite [43]. Besides, some Mn-ores showed the oxygen uncoupling property when the iron content was high [44].

Less is known about the reactivity of bixbyite and spinel phases with reducing agents, e.g. H_2 , CO or CH_4 , as well as the capability to regenerate the bixbyite phase. Reaction of reducing gases with lattice oxygen in bixbyite can also proceed in a similar way than that for spinel shown in reactions (R2)-(R4). In fact, this mechanism could be also relevant when the gas concentration is relatively high [45]. Nevertheless, the focus has been placed on the oxygen uncoupling mechanism of bixbyite because of its high potential to highly convert a solid fuel [4].

In a previous work, several Mn-Fe mixed oxides prepared by mechanical mixing followed by pelletization by pressure have been evaluated as oxygen carriers [28]. Particles with composition $(\text{Mn}_{0.77}\text{Fe}_{0.23})_2\text{O}_3$ calcined at 1223 K showed good reactivity and crushing strength (2.7 N) to be used as oxygen carrier. Then, these particles were prepared by an industrial method, i.e. spray drying, to be used in a CLC unit [35]. Severe sintering conditions (1623 K for 2 h) were required to produce particles with high enough crushing strength (1.7 N), and these particles exhibited magnetic properties ($\mu_r = 2.5$). However, the capability to regenerate the bixbyite was hindered. Considering that bixbyite should be formed to take advantage of the oxygen uncoupling mechanism, it was concluded that this material was not valid for the CLOU process, although high combustion efficiency was achieved owing to its high reactivity with regard to CLC reactions; see reactions (R2)-(R4). The reactivity of Mn-Fe mixed oxides was improved by doping with Ni, but oxygen uncoupling capability was not reported [46].

Recently, it was determined that Mn-Fe particles doped with 7 wt% TiO_2 showed oxygen uncoupling capability, high reactivity, high mechanical strength and magnetic properties [36]. Materials calcined at 1473 K and with a Mn/(Mn+Fe) of 0.5 and 0.66 were identified as promising oxygen carriers for CLaOU. Particles with Mn/(Mn+Fe) = 0.66, with a crushing strength of 3.8 N and relative magnetic permeability of $\mu_r = 7.8$, would be preferred due to the narrow gap in the phase diagram between the spinel and bixbyite phases, which facilitates a higher oxidation to bixbyite [26].

Despite the extensive bibliography on the development of Mn-Fe mixed oxide materials with oxygen uncoupling capability, experience in CLC units is limited to the combustion of natural gas in a 300 W_{th} unit [47]. However, operation failed due to the high attrition index of the material, which was found in most of Mn-Fe developed materials [26]. In this sense, the Mn-Fe-Ti material previously developed had suitable properties to be used in a

CLC unit with solid fuels. Prior to this, it is fundamental to determine a suitable window of operating conditions at which this material should be tested, which has not been determined for those Mn-Fe mixed oxides as far as the authors' knowledge.

The objective of this work was to perform a deep evaluation of a Mn-Fe-Ti mixed oxide as oxygen carrier prepared by an industrially scalable method such as spray drying. An optimized composition with a Mn:Fe molar ratio of 0.66:0.34 was selected, including 7 wt% TiO₂ to achieve the following stoichiometric formula: (Mn_{0.66}Fe_{0.34})₂O₃·(TiO₂)_{0.15}. Physical and chemical characterization was carried out as a function of sintering temperature in order to achieve particles with suitable reactivity for the processes involved in CLC, mechanical strength and magnetic properties. Suitable operating conditions for the redox processes were determined, paying special attention on the oxidation conditions for the regeneration of bixbyite. It is noteworthy to analyze the ability to regenerate the bixbyite phase, because the oxygen uncoupling capability cannot be exploited if bixbyite was not formed during the oxidation stage.

2. Experimental

2.1. Oxygen carrier

A batch of 5 kg of oxygen carrier material was prepared by the Flemish Institute for Technological Research (VITO) by the spray-dried method obtaining particles in the 0.1–0.3 mm size interval. The mixture of the solid precursors consisted of 60 wt% Mn₃O₄ (Strem Chemical Inc.), 33 wt% Fe₂O₃ (Panreac Prs.) and 7 wt% TiO₂ (Panreac Prs.) in order to obtain the desired stoichiometry of (Mn_{0.66}Fe_{0.34})₂O₃·(TiO₂)_{0.15}, which was previously optimized with particles prepared by pelletization by pressure [36]. The spray dried particles, from now on labelled Mn66FeTi7, were subjected to a sintering step in air at a temperature interval of 1223–1473 K for 2 hours. Subsequently, the samples were

slowly cooled down until room temperature in order to promote the formation of bixbyite type phases.

2.2. Physicochemical characterization of oxygen carrier particles

Measurements of crushing strength were calculated taking the average value of the fracture force on 20 particles using a Shimpo FGN-5X force gauge. Attrition resistance was determined using a three-hole air jet attrition tester ATTRI-AS (Ma.Tec. Materials Technologies Snc) configured according to the ASTM-D-5757 standard [48], and the Air Jet Index (AJI) was obtained with the procedure previously described [49]. A Quantachrome PoreMaster 33 device was used to measure the porosity of the particles by means of Hg intrusion. A Bruker AXS D8 Advance X-ray diffractometer equipped with an X-ray source with a Cu anode and an energy-dispersive one-dimensional detector was used in order to determine the crystalline phases. Crystalline phases were assigned by means of DIFFRAC.EVA software according to JCPDS database. Chemical species in the crystalline part of the solid were quantified by using TOPAS software. Micrograph images of the particles were obtained by means of a Scanning Electron Microscope (SEM) Hitachi S-3400 N. Relative magnetic permeability (μ_r) was measured in a Bartington Instruments MS3 magnetic susceptibility meter coupled with an MS2G single frequency sensor; see Annex for more information.

2.3. Thermogravimetric analysis

A thermogravimetric analyzer (TGA) CI Electronics type was used to determine both the oxygen transport capacity and the reactivity of Mn₆₆FeTi₇ particles. The solid sample (~50 mg) was placed in a platinum mesh basket to minimize diffusional effects, and the flow of reacting gases was 25 L/h (STP), akin to previous work [36].

Temperature programmed tests were carried out to determine total oxygen transport capacity ($R'_{OC,exp}$) and uncoupled oxygen transport capacity ($R^{ou}_{OC,exp}$). Two redox cycles were carried out by alternating temperature programmed reduction (TPR: heating at 20 K/min from 673 K up to 1273 K) and temperature programmed oxidation (TPO: cooling at

8 K/min from 1273 K to 673 K). Highly-pure N₂ or CH₄ was used during TPR, while 5 or 21 vol% O₂ in N₂ was used during TPO.

Isothermal redox cycles were performed to analyze the reactivity of the material under both CLOU and CLC conditions. First, the solid sample was heated in air from room temperature up to desired temperature (1073–1273 K). Afterward, redox cycles started. Gaseous oxygen released in CLOU mode was evaluated in 100 vol% highly-pure N₂ for 2 min. For CLC mechanism, the reduction of the oxygen carrier was performed in 15 vol% H₂, 15 vol% CO or 15 vol% CH₄ for 2 min. 20 vol% CO₂ or 20 vol% H₂O was respectively added to CO or CH₄ in order to prevent carbon formation inside the TGA reactor. Air or diluted air in N₂ (5, 10, 15 and 21 vol% O₂) was used during the oxidation step for 5 min. In some cases, the reduction period was increased to 5 min and the oxidation lasted 30 min with the objective of determining the optimum conditions in order to take advantage of the oxygen uncoupling properties of the material.

2.4. Data evaluation

The mass fraction of oxygen transferred between the oxidized and reduced states is evaluated by experimental oxygen transport capacity ($R_{OC,exp}^i$) in TGA tests:

$$R_{OC,exp}^i = \frac{m_o^i - m_r^i}{m_{bix}} \quad (1)$$

where m_o^i and m_r^i are the mass of the oxygen carrier at the end of the oxidation and reduction steps, respectively. m_{bix} is the initial mass of the sample assuming full oxidization to bixbyite. This means that $m_o^i < m_{bix}$ when the oxygen carrier is not fully oxidized to bixbyite. Depending on the redox system i considered, three different $R_{OC,exp}^i$ parameters can be defined: (1) for oxygen uncoupling ($R_{OC,exp}^{ou}$), m_o^i and m_r^i are the mass of the sample after oxidation and fully reduced to spinel, respectively; (2) for CLC

conditions ($R_{OC,exp}^g$), m_o^i and m_r^i are the mass of the sample in the spinel form and after reduction period with a reducing gas; and (3) the total oxygen transport capacity considers the reduction from the oxidized state both by oxygen uncoupling and reducing gas, being easily calculated as $R_{OC,exp}^t = R_{OC,exp}^{ou} + R_{OC,exp}^g$.

The progress of the oxidation state of the oxygen carrier is evaluated through the mass-based conversion, ω .

$$\omega = \frac{m}{m_{bix}} \quad (2)$$

where m is the instantaneous mass of the sample. The rate of reaction i (i : *ox* for oxidation; i : *ou* for oxygen uncoupling; or i : *red* for reduction) was calculated by:

$$r_i = \left(\frac{d\omega}{dt} \right) \quad (3)$$

The reactivity of the oxygen carrier particles was assessed by calculating the normalized *Rate index* [50]:

$$Rate\ index\ (\% / \min) = 60 \cdot 100 \cdot \left(\frac{d\omega^i}{dt} \right) \quad (4)$$

where ω^i can be referred to the oxygen uncoupling (i : *ou*, in N_2), the reduction with a gaseous fuel (i : *g*, in 15 vol% gas) or the oxidation reaction (i : *o*, in 10 vol% O_2).

3. Results and discussion

3.1. Determination of the optimal sintering procedure

Mn66FeTi7 particles were subjected to a sintering process in air for 2 hours at different temperatures from 1223 K to 1473 K in order to obtain particles with suitable mechanical, chemical and magnetic properties. The main characteristics of the particles are included in Table 1. Increasing sintering temperature involved a significant improvement of the

mechanical properties achieving a crushing strength value of 2 N at 1473 K, which is an adequate value for an oxygen carrier [49,50]. The increase in the crushing strength is directly related to the loss of porosity of the particles.

Table 1. Physicochemical properties of Mn₆₆FeTi₇ particles prepared by spray-drying and sintered at different temperatures.

			Sintering temperature (K)			
			1223	1323	1373	1473
Crushing strength (N)			0.5	0.6	1.0	2.0
Porosity (%)			46.2	41.9	28.3	9.5
Relative magnetic permeability, μ_r (-)			1.0	1.0	1.3	1.6
XRD main crystalline phases (%)	Bixbyite phases	Mn ₂ O ₃	30.2	30.2	42.6	46.2
		MnFeO ₃	65.1	65.0	38.2	30.4
		Fe ₂ O ₃	-	-	7.5	4.4
		Total bixbyite	95.3	95.2	88.3	81.0
	Spinel phases	Fe ₃ O ₄	-	-	5.3	8.9
		Mn _{1.58} Fe _{1.42} O ₄	-	-	3.3	-
		Fe ₂ TiO ₄	-	-	-	3.2
		Mn ₃ O ₄	-	-	-	1.3
		Total spinel	0.0	0.0	8.6	13.4
	TiO ₂		4.7	4.8	3.1	5.6

Fig. 1 shows the SEM micrographs of particles sintered at 1223 K and 1473 K. The increase of the sintering temperature modified the external morphology of Mn₆₆FeTi₇ particles. At 1223 K, the particles showed a rugose and porous appearance, which was modified at 1473 K by arising a set of superposed bigger crystals and the disappearance of visible pores.

XRD analysis showed that particles sintered at 1223 K and 1323 K were essentially formed by bixbyite-type phases. Compounds with spinel lattice structure appeared in particles sintered at higher temperatures at the expense of a decrease of the proportion of bixbyite phases. In addition, when the solids were sintered at 1373 K or 1473 K a proportion of iron atoms was dissociated from the initial (Mn_xFe_{1-x})₂O₃ phases to form single iron oxides, i.e., Fe₂O₃ and Fe₃O₄, or Fe-Ti mixed oxides. As a consequence, the bixbyite phase was manganese enriched.

Fig. 1. SEM pictures of Mn₆₆FeTi₇ particles sintered at 1223 K or 1473 K.

With regard to the magnetic behavior, particles began to show a relevant magnetism when were sintered at 1373 K. Then, it was improved by sintering at 1473 K. It is believed that magnetic properties are related to the appearance of spinel-type phases, such as $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ or Fe_3O_4 , even in the oxidized particles. This fact suggests that this material could maintain permanent magnetic properties after redox cycles in a CLC unit. This would allow particles to be easily recovered from ash in the draining stream for its reuse in the CLC rig.

The properties shown by the Mn₆₆FeTi₇ material prepared by spray drying were different to those of this material prepared by pelletization by pressure [36] or the Mn₇₇Fe material previously developed, with the stoichiometric composition $(\text{Mn}_{0.77}\text{Fe}_{0.23})_2\text{O}_3$ [35]. Thus, the crushing strength for the material prepared by spray drying (2 N) was lower than that for the material prepared by pelletization by pressure (3.8 N). This is a common finding when particles prepared by both methods are compared, for example comparing Cu-based materials [51,52], but the spray drying is a scalable industrial method. In addition, Mn₆₆FeTi₇ was produced by exchanging some Mn in $(\text{Mn}_{0.77}\text{Fe}_{0.23})_2\text{O}_3$ by Ti. The lower Mn:Fe molar ratio and/or the presence of Ti in Mn₆₆FeTi₇ entailed a decrease of the sintering temperature required to produce particles with magnetic properties from 1498 K

in Mn77Fe to 1373 K, and to produce particles with high enough crushing strength from 1623 K to 1473 K. Mn77Fe particles prepared by spray drying calcined at 1473 K showed a crushing strength of 0.4 N, while no magnetic properties were observed. In order to obtain particles with high mechanical strength and magnetic properties, the calcining temperature should be increased up to 1623 K. Magnetic properties in Mn77Fe were mostly given by the presence of Mn-Fe spinel, while it was due mostly to Fe₃O₄ in Mn66FeTi7. In addition, the oxygen uncoupling capability of the selected Mn77Fe material sintered at 1623 K was lost due to the low capability for the regeneration of the bixbyite phase in air. But a high fraction of bixbyite was observed in Mn66FeTi7 particles, which suggests that bixbyite regeneration was possible in this case. Therefore, the oxygen uncoupling capability of the Mn66FeTi7 material could be exploited. These results are in agreement with those observed by Abián et al. with particles prepared by mechanical mixing [36].

In order to produce particles with high enough mechanical strength and magnetic properties, Mn66FeTi7 particles sintered at 1473 K were selected for a further evaluation. In order to evaluate the resistance of attrition under fluidization conditions, the Air Jet Index (AJI) was determined. The AJI value for these particles was 1 %, which can be compared to the threshold value of 5 % previously suggested to consider an oxygen carrier suitable for its use in fluidized bed reactors [49].

3.2. Oxygen transport capacity assessment

The oxygen transport capacity of the sintered Mn66FeTi7 material was determined by alternating TPR and TPO, as it was described in Section 2.3. TPR in nitrogen was used to determine oxygen transport capacity for the oxygen uncoupling process ($R_{OC,exp}^{ou}$) following reaction (R1); see Fig. 2(a). Considering the bixbyite fraction reported in Table 1 (81 %), the initial value of the mass-based conversion was estimated to be $\omega_0 = 0.994$; see Eq. (2).

The complete reduction of bixbyite to spinel was achieved during the TPR stage. However, the oxidation was highly dependent on the oxygen concentration. Regeneration to the initial state was achieved by supplying air in the oxidizing step. The oxidation of spinel started at 1265 K and the initial oxidation state was fully recovered at 1143 K. The experimental oxygen transport capacity for oxygen uncoupling was $R_{OC,exp}^{ou} = 0.026$, which is the 81 % of the theoretical value of $R_{OC}^{ou} = 0.032$ assuming complete oxidation from spinel to bixbyite in Mn66FeTi7. However, very limited oxidation was obtained with an oxidizing atmosphere of 5 vol% O₂. The oxidation was delayed up to the temperature decreased to 1218 K, followed by a slow regeneration of the bixbyite, which was negligible when the reactor temperature dropped below 983 K. The experimental oxygen transport capacity obtained at this condition was $R_{OC,exp}^{ou} = 0.006$, which implied a regeneration conversion degree of only ~20 %. This phenomenon suggests a limited capability to regenerate the bixbyite by using 5 vol% O₂.

Fig. 2. Mass-based conversion (ω) of Mn66FeTi7 and reacting temperature (----) variation with time during consecutive TPR-TPO cycles. Reduction: (a) 100 vol% highly-pure N₂; (b) 15 vol% CH₄ + 20 vol% H₂O. Oxidation: 21 vol% O₂ (—) or 5 vol% O₂ (—).

Fig. 2(b) shows the mass-based conversion obtained in TPR-TPO cycles when reduction was promoted in presence of CH₄. Thus, bixbyite and spinel initially present in the oxygen

carrier were reduced to mangano-wüstite, $(\text{Mn}_x\text{Fe}_{1-x})\text{O}$, in the TPR stage. Subsequently, the oxidation of mangano-wüstite was performed in 5 or 21 vol% O_2 during the TPO stage. Two differentiated steps with great differences in the oxidation rates were observed. Quick and complete oxidation to spinel phase following reaction (R5) was observed regardless the oxygen concentration. Afterward, the spinel oxidation to bixbyite was slower and it was highly affected by the oxygen concentration, as it was above discussed for the TPO stage when the oxygen uncoupling capability was evaluated; see Fig. 2(a). This behavior was in agreement with that observed by Lambert et al. [30].

When the oxygen carrier was oxidized in air, the experimental total oxygen transport capacity was $R'_{OC,\text{exp}} = 0.088$, which was somewhat lower than the theoretical value of $R'_{OC} = 0.094$ [36]. A lower value of $R'_{OC,\text{exp}} = 0.068$ was achieved oxidizing in 5 vol% O_2 because of the limited spinel oxidation to bixbyite. In this case, most of the oxygen was transferred by means of the gas reaction with lattice oxygen in the solid (CLC mode).

3.3. Behavior of the oxygen carrier particles during consecutive redox cycles

Ten redox cycles were performed at 1123 K in TGA to evaluate the possible variation of the particles reactivity with the cycle number. Fig. 3 shows the mass-based conversion of the oxygen carrier along 10 redox cycles in TGA at 1123 K. Initially, a fraction of the oxygen was evolved during the inert step in N_2 via oxygen uncoupling mechanism. Afterward, the reaction rate was significantly increased by the reduction with 15 vol% CH_4 , which suggests that it is faster than the oxygen uncoupling rate. Nevertheless, the contrary behavior could be found for low values of gas concentration [45]. In any case, the oxygen uncoupling mechanism could be of great relevance for the combustion of solid fuels. Then, reduction of the spinel would proceed uniquely by reaction of CH_4 with lattice oxygen, as no oxygen uncoupling capability would be associated to the spinel phase.

Spinel was quickly regenerated during oxidation in air, but only partial regeneration of the

bixbyite was achieved. Limited reduction and oxidation conversion were observed because these steps were stopped before the completion of the reactions.

Fig. 3. Mass-based conversion (ω) of Mn66FeTi7 during 10 redox cycles in the TGA at 1123 K. Stages for each cycle: (1) highly-pure N₂ for 2 min; (2) reduction 15 vol% CH₄ + 20 vol% H₂O for 2 min; (3) highly-pure N₂ for 2 min; (4) oxidation in air for 5 min.

In subsequent cycles, a mass loss of the particles was recorded during the inert period in N₂ owing to the oxygen released by the bixbyite phase decomposition. Complete conversion of bixbyite to spinel was achieved during this stage. During the first 5 cycles, a slight activation was observed both for the reduction stage with CH₄ and for the oxidation of mangano-wüstite to spinel. So, the normalized *Rate index* for the mangano-wüstite oxidation increased from 4 %/min in the first cycle to 7 %/min in the cycle 5-6. Afterward, the redox reactivity was maintained constant.

In addition to the increase of reactivity with the redox cycles, some changes in the crystalline phases of the solid were observed by XRD. Fig. 4 shows the evolution of the fraction of every crystalline phase grouped by: (1) bixbyite, characterized by compounds with Mn³⁺ and Fe³⁺ cations; (2) spinel, characterized by compounds including Mn³⁺/Mn²⁺ and/or Fe³⁺/Fe²⁺; (3) mangano-wüstite, characterized by the presence of Mn²⁺ and Fe²⁺;

and (4) hexagonal, characterized by Fe-Ti compounds.

Fig. 4(a) shows the evolution of crystalline phases during the oxygen uncoupling process. In this case, no major changes were observed in the crystalline phases with the redox cycles, prevailing bixbyite and spinel phases in the oxidized and reduced states, respectively. Some spinel was found in the oxidized state, which would confer magnetic properties upon the particles. In addition, some hexagonal phase appeared with the redox cycles, suggesting that some Fe migrated from the Mn-Fe mixed oxide to a Fe-Ti phase.

Fig. 4. Quantification of crystalline phases of Mn₆₆FeTi₇ samples before and after experimentation in TGA, as shown in Fig. 3.

When the oxygen carrier reacted with CH₄, relevant changes were found during the first cycles; see Fig. 4(b). Thus, a lower fraction of mangano-wüstite was generated during the first reduction. Spinel remained as the main crystalline phase, which agrees with the

limited reduction conversion observed in this first cycle. Interestingly, the formation of Fe-Ti compounds was also relevant, which suggests that the migration of Fe was promoted during the reduction of spinel to mangano-wüstite. In the subsequent cycles, bixbyite could be mostly regenerated in air, but Fe atoms were also found together Ti^{4+} cations forming hexagonal close packing structures. During reduction, the presence of mangano-wüstite phases was improved with the redox cycles. In addition, Ti^{4+} cations were dissolved into a cubic lattice, being integrated together with Mn and Fe into an ulvöspinel structure; i.e., $(\text{Mn}_x\text{Fe}_{1-x})_2\text{TiO}_4$. This result agrees with that observed for Fe_2TiO_4 samples doped with manganese oxide [53]. Ti^{4+} cations have preference for the octahedral sites into the cubic lattice of ulvöspinel, which entails the expansion of the unit cell dimension because of its higher ionic radius. This expansion would aid to improve the reduction of the Mn^{3+} cations present into the octahedral positions of the MnFe_2O_4 [54], which could be related with the increase of the reactivity with CH_4 observed with the redox cycles; see Fig. 3.

The observed phases agree with the expected phases derived from theoretical calculations; see Fig. 5. In this regard, different segregated Fe-Ti phases can be generated at reducing conditions, i.e. conditions with low partial pressure of oxygen. The oxidation of these segregated phases can lead to the formation of pseudobrookite, Fe_2TiO_5 . However, the capability to recover the bixbyite phase is not lost after a long oxidation period, as it is shown in the up-left corner in Fig. 5. This fact agrees with the results obtained in TGA at temperatures lower than 1123 K; see Annex. In real conditions, the time for oxidation would be limited and it is expected to be not enough to achieve complete oxidation at the temperature and oxygen partial pressure existing in the air reactor. Therefore, it can be anticipated that the phases present in reacted particles in a CLC unit would be closer to that shown in Fig. 4.

Fig. 5. Mn-Fe-Ti-O phase diagram as a function of the temperature and the partial pressure of O₂ for the Mn₆₆FeTi₇ material. Solid phases were obtained with FactSageTM software by using FToxid database [55]. The narrowest areas between the most relevant areas correspond to a mixture of the adjacent phases.

3.4. Comprehensive study of the oxygen uncoupling capability

It is well known that the conversion of a solid fuel, e.g. coal or biomass, is improved with oxygen carriers showing oxygen uncoupling capability [4]. In the case of Mn-Fe mixed oxide materials, the oxygen uncoupling capability depends on the degree of oxidation of the spinel to bixbyite. In this sense, a comprehensive analysis of the bixbyite regeneration is required in order to optimize the oxygen transport capability by oxygen uncoupling. Moreover, oxygen releasing capability by decomposition of bixbyite to spinel in an inert environment will be also evaluated.

3.4.1. Regeneration of bixbyite phase

Five redox cycles were carried out in a TGA to evaluate the regeneration of bixbyite from spinel. CH_4 was used during the reduction stage in order to guarantee full reduction of bixbyite. Then, different O_2 concentration (5, 10, 15 and 21 vol%) and reacting temperatures between 1073 and 1273 K were used for the oxidation stage. The mass-based conversion evolution vs. time during the 5th oxidation half-cycle was selected for this evaluation; see the Annex. For the purpose pursued in this section, the oxidation of spinel to bixbyite was only considered. Interestingly, an induction period was observed at the beginning of the spinel oxidation followed by an increase of the oxidation rate. This phenomenon is often found in manganese rich Mn-Fe mixed oxides because the spinel oxidation follows a nucleation and nuclei growth model [56]. A detailed description of the determination of both the induction period and the spinel oxidation rate can be found in the Annex.

Fig. 6 depicts the induction period length as a function of the oxygen concentration and reacting temperature. On the one hand, the induction period length decreases at increasing O_2 concentration independently of the temperature, which might be explained by the improvement of the nucleation process happening during the first step of the spinel oxidization to bixbyite [57]. Thus, the increase of O_2 partial pressure could drive the formation of more cation vacancies during the transformation of the cubic structure from spinel to bixbyite. On the other hand, the induction period increases as temperature increases. This behavior is closely related to the strong reaction rate decrease at high temperatures, which is discussed below. It is interesting to note that the induction period in some circumstances could be much longer than the residence time of the oxygen carrier in the air reactor, usually considered being less than 60 s [58]. Of course, the reaction temperature must be below 1200 K to avoid an extremely long induction period.

Fig. 6. Spinel oxidation rate ($r_{ox}^{sp \rightarrow bix}$) and induction period length for the spinel oxidation to bixbyite as a function of the temperature and the partial pressure of O₂. Values obtained in TGA during 5th oxidation half-cycle. Reduction half-cycle in 15 % CH₄ + 20 % H₂O.

Fig. 6 also shows that the spinel oxidation rate increased with the partial pressure of O₂ independently of the temperature checked. However, a maximum value in the oxidation rate was observed as a function of the temperature for each O₂ concentration tested. The greatest oxidation rate was obtained at 1148 K when the spinel was oxidized in air, i.e., 21 vol% O₂. The temperature at which the maximum oxidation rate was observed decreased as the O₂ partial pressure decreased. This behavior can be explained in terms of the effect of temperature on the kinetic constant, $k(T)$ and the oxygen concentration at equilibrium conditions, $C_{O_2,eq}$:

$$\left(r_{ox}^{sp \rightarrow bix}\right) = \overbrace{f[k(T)]}^{\text{kinetic term}} \cdot \overbrace{f\left(C_{O_2} - C_{O_2,eq}\right)}^{\text{driving force}} \cdot \overbrace{f\left(X_{OC}\right)}^{\text{reaction model}} \quad (5)$$

Kinetic constant, k , should increase with the temperature. On the contrary, *driving force* for

the oxidation, i.e. $C_{O_2} - C_{O_2,eq}$, decreases with temperature because of the oxygen concentration increase at equilibrium, $C_{O_2,eq}$. Thus, if a low temperature is considered, at which $C_{O_2} \gg C_{O_2,eq}$, the kinetic term dominates the effect of the temperature on the oxidation rate, observing an increase of the oxidation rate with the temperature. At increasing temperature, $C_{O_2,eq}$ approaches to the bulk oxygen concentration, C_{O_2} , affecting negatively the reaction rate. This means that the oxidation rate decreases with the temperature increase when the negative effect of the *driving force* is higher than the positive effect of the *kinetic term*. The combination of both effects defines the temperature at which the maximum oxidation rate is achieved.

Significant differences were found when using 5 vol% O_2 in comparison to the rest of O_2 concentrations checked. In this case, the reaction rate would be limited by setting an O_2 concentration too close to the equilibrium concentration. Therefore, it becomes extremely important to control the partial pressure of O_2 during the oxidation of the spinel phase. In the practice, this fact will depend on the air excess supplied to the air reactor of a CLC unit. Considering jointly the length of the induction period and the bixbyite regeneration rate, it seems advisable to set an O_2 concentration at the air reactor higher than 5 vol%. Nevertheless, the early spinel oxidation will be boosted close to the air inlet, where the O_2 concentration would be high enough to avoid a relevant induction period. Once the spinel oxidation has begun, the oxidation will proceed at any position in the air reactor without the necessity of a long induction period, even if the O_2 concentration was low. With this in mind, the induction period would be minimized and the spinel oxidation rate should be maximized by oxidizing at a temperature in the 1123-1173 K interval. In addition, the oxygen concentration can be increased in the whole air reactor by increasing the air excess ratio. The permissible air excess should be determined considering the whole enthalpy balance of the CLC unit.

3.4.2. Oxygen uncoupling behavior of bixbyite phase

The oxygen uncoupling capability of the Mn-Fe mixed oxides is related to the presence of bixbyite phase; see Reaction (R1). Previous works have shown that the oxygen uncoupling rate of bixbyite is highly influenced by temperature [28,36]. However, it must be considered that the temperature and the O₂ concentration during the oxidation stage affect the fraction of bixbyite being regenerated, which could in turn affect the O₂ release by the oxygen uncoupling mechanism. To evaluate this effect, the oxygen uncoupling rate of bixbyite ($r_{ou}^{bix \rightarrow sp}$) was determined as a function of the existing conditions in the previous oxidation stage.

Fig. 7(a) shows the oxygen uncoupling rate as a function of the O₂ partial pressure and temperature during the oxidation stage. It must be considered that isothermal cycles were carried out, i.e. the temperature during the oxygen uncoupling process was the same than during the oxidation. Clearly, an increase of the O₂ partial pressure during oxidation led to an increase of the oxygen releasing rate in the subsequent oxygen uncoupling reaction, which was more marked at temperature above 1173 K. This fact implies that the oxygen uncoupling rate increased when the bixbyite regeneration was improved by increasing the O₂ concentration. In addition, the increase of the temperature has a positive effect on the oxygen uncoupling rate up to a maximum value of the reaction rate is reached. The temperature at which this maximum is observed depends on the O₂ partial pressure used during oxidization stage. The decrease of the oxygen uncoupling rate at high temperatures is closely related to the decrease of the conversion of spinel to bixbyite at these temperatures, as it was evaluated in Section 3.4.1. To observe this effect, the oxygen transport capacity for the oxygen uncoupling reaction ($R_{OC,exp}^{ou}$) was determined as a function of the O₂ partial pressure and temperature during oxidation; see Fig 7(b). The oxygen transport capacity for oxygen uncoupling was improved when either the O₂ partial

pressure was increased or the fuel reactor temperature was decreased. Both facts are related to the enhancement of the bixbyite regeneration by optimizing the operating conditions in the air reactor. Maximum values around $R_{OC,exp}^{ou} = 0.032$ were achieved at lower fuel reactor temperatures for O_2 partial pressure greater than 0.05 atm.

Fig. 7. (a) Oxygen uncoupling rate of bixbyite ($r_{ou}^{bix \rightarrow sp}$) and (b) oxygen transport capacity $R_{OC,exp}^{ou}$ as a function of the O_2 partial pressure and temperature in the oxidation stage. The temperature for the bixbyite decomposition was equal to the oxidation temperature.

In summary, Fig. 7 shows that the oxygen uncoupling capability is highly dependent on the oxidation conditions. So, the temperature and air excess in the air reactor are key parameters to maximize the oxygen transport capacity via oxygen uncoupling mechanism. Considering the coupled effect of temperature on the oxygen uncoupling and oxidation reactions, it can be concluded that the determination of the fuel reactor operating conditions must be done jointly to the evaluation of the optimum operating conditions in the air reactor to properly regenerate the bixbyite phase. An enthalpy balance to the whole CLC unit should be done to determine the suitable operating conditions both for the air and fuel reactors.

3.5. Evaluation of spinel reduction by gas-solid reaction

In addition to the oxygen uncoupling capability, the Mn-Fe mixed oxide can react with gaseous products generated during coal conversion to gas (e.g., H_2 , CO or CH_4), which is characteristic of the *i*G-CLC process. Owing to spinel phase is quickly regenerated regardless the oxidizing conditions, the reduction of spinel, i.e. $(Mn_xFe_{1-x})_3O_4$, to mangano-wüstite, i.e. $(Mn_xFe_{1-x})O$, is here evaluated; see reactions (R2)-(R4). In order to compare the reactivity of the Mn66FeTi7 material with available values in the literature for other oxygen carriers, redox cycles were performed in TGA at 1223 K by reducing with 15 vol% either H_2 , CO or CH_4 , and oxidizing in air.

Fig. 8. Normalized *Rate index* of Mn66FeTi7 particles with different gases and oxygen transport capacity (R_{OC}^g) considering spinel/mangano-wüstite redox system. Data for other oxygen carriers have been included for comparison purposes [35,59].

Fig. 8 shows the normalized *Rate index* for the reaction of Mn66FeTi7 with different gases and its oxygen transport capacity (R_{OC}^g), considering the spinel/mangano-wüstite redox system. The *Rate index* and R_{OC}^g values for other oxygen carriers used in the combustion of solid fuels are also included for comparison purposes [35,59]. The reactivity of the

Mn₆₆FeTi₇ material was similar to that shown by ilmenite, which can be considered as a reference oxygen carrier for the combustion of solid fuels [4]. But differences can be found compared to other low cost Fe-based materials. Thus, the *Rate index* of Mn₆₆FeTi₇ against H₂ and CO is lower than those found for an iron ore or Fe-enriched sand fraction (Fe-ESF), similar against CH₄, or even higher for the oxidation. Nevertheless, Mn₆₆FeTi₇ is able to transport a greater amount of oxygen, i.e., R_{oc}^g is higher. In this sense, the required solids circulation rate would be lower. As a result, higher CO₂ capture efficiencies would be expected because the solids residence time inside the fuel reactor would be increased. Moreover, its reactivity against H₂, CO or CH₄ is lower in comparison with the previously tested Mn₇₇Fe material [35]. However, as much the Mn₇₇Fe material as the alternative low-cost materials shown in Fig. 8 do not show oxygen uncoupling capability [18,35]. Therefore, considering the relevance of the oxygen uncoupling mechanism in order to achieve complete combustion of solid fuels such as coal or biomass [22,24], the oxygen uncoupling capability of the Mn₆₆FeTi₇ material must be promoted and exploited in order to maximize the combustion efficiency.

4. Conclusions

A Mn-Fe mixed oxide doped with TiO₂ and stoichiometric formula (Mn_{0.66}Fe_{0.34})₂O₃·(TiO₂)_{0.15} and named Mn₆₆FeTi₇, was developed as an oxygen carrier with oxygen uncoupling capability and magnetic behavior both in the oxidized and reduced states. An optimum calcination temperature of 1473 K was determined for this material, in which properties as the mechanical strength, reactivity, oxygen uncoupling capability and magnetic behavior were evaluated.

The Mn₆₆FeTi₇ material was mainly composed by bixbyite and spinel phases, in the oxidized state. Both bixbyite and spinel can be reduced with gaseous fuels (i.e., H₂, CO,

and CH₄) to mangano-wüstite, showing a high total oxygen transport capacity of $R'_{OC} = 0.088$. The reactivity of Mn₆₆FeTi₇ particles with these gaseous fuels was similar, or even lower, to that shown for other low cost materials.

Nevertheless, this material shows oxygen uncoupling capability, i.e. releases gaseous oxygen at high temperature during bixbyite decomposition to spinel. The oxygen release rate depends on the spinel conversion to bixbyite achieved in the previous oxidation stage, which is highly influenced by the O₂ concentration and temperature. A relevant induction period was observed at low O₂ concentration and at temperatures above 1223 K, which could limit the bixbyite regeneration considering the residence time of solids in the air reactor. Thus, the oxidation temperature was limited to the 1123–1173 K interval to maximize the oxygen uncoupling capability of the material.

Results presented in this work are of great relevance for the optimization of a CLC unit with the Mn₆₆FeTi₇ material. In comparison with the state of the art of Fe- or Mn-based oxygen carriers, the performance of the fuel conversion in a Chemical Looping Combustion (CLC) unit could be improved using the Mn₆₆FeTi₇ material by optimizing operating conditions in the air reactor in order to promote its oxygen uncoupling capability in the fuel reactor. In this sense, the analysis of the oxidation reaction becomes highly relevant when evaluating the oxygen uncoupling capability.

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Nomenclature

C_{O_2}	reacting oxygen concentration ($\text{mol}\cdot\text{m}^{-3}$)
$C_{O_2,eq}$	oxygen concentration at equilibrium ($\text{mol}\cdot\text{m}^{-3}$)
k	chemical reaction kinetic constant ($\text{m}^3\cdot\text{mol}\cdot\text{s}^{-1}$)
m	instantaneous mass of oxygen carrier (kg)
m_{bix}	mass of the oxygen carrier completely oxidized to bixbyite (kg)
m_o^i	mass of oxidized sample of oxygen carrier for the mechanism i ($i = ou$ or g) (kg)
m_r^i	mass of reduced sample of oxygen carrier for the mechanism system i ($i = ou$ or g) (kg)
$P(O_2)$	partial pressure of oxygen (atm)
$R_{OC,exp}^g$	oxygen transport capacity by the reaction between spinel and mangano-wüstite obtained experimentally in TGA (kg oxygen per kg of oxygen carrier)
$R_{OC,exp}^{ou}$	oxygen transport capacity by the oxygen uncoupling reaction between bixbyite and spinel obtained experimentally in TGA (kg oxygen per kg of oxygen carrier)
$R_{OC,exp}^t$	total oxygen transport capacity of solid between bixbyite and mangano-wüstite obtained experimentally in TGA (kg oxygen per kg of oxygen carrier)
$R_{OC,max}^g$	theoretical maximum oxygen transport capacity of solid between spinel and mangano-wüstite (kg oxygen per kg of oxygen carrier)
$R_{OC,max}^{ou}$	theoretical maximum oxygen transport capacity of solid between bixbyite and spinel (kg oxygen per kg of oxygen carrier)
$R_{OC,max}^t$	theoretical maximum total oxygen transport capacity of solid between bixbyite and mangano-wüstite (kg oxygen per kg of oxygen carrier)
$r_{ou}^{bix\rightarrow sp}$	bixbyite decomposition rate through oxygen uncoupling mechanism (s^{-1})
$r_{ox}^{sp\rightarrow bix}$	spinel oxidation rate to bixbyite (s^{-1})
T	temperature (K)
X_{OC}	oxygen carrier conversion (-)

Greek symbols

μ_r	relative magnetic permeability (-)
ω	mass-based conversion (-)

Acronyms

CLaOU	Chemical Looping <i>assisted by</i> Oxygen Uncoupling
CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
iG-CLC	<i>in-situ</i> Gasification Chemical Looping Combustion
SEM	Scanner Electron Microscope
XRD	X-Ray Diffraction
STP	Standard Temperature and Pressure
TGA	Thermogravimetric Analyzer
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction

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ANNEX

A.1. Assessment of the oxidation stage by TGA tests.

TGA experiments were conducted in order to calculate the spinel oxidation rate to bixbyite as a function of the temperature and partial pressure of O₂. These tests were performed at temperatures between 1073 and 1273 K (at intervals of 25 K) and using different O₂ concentration (5, 10, 15 and 21 vol%). For every condition, five redox cycles were carried out supplying CH₄ for 15 min, and air or diluted air for 30 min during the reduction and oxidation stage, respectively. Fig. A1 show the mass-based conversion vs. time curves for the 5th oxidation half-cycle at each temperature studied.

From these figures, the length of the induction period and the spinel oxidation rate to bixbyite was determined. As an example, Fig. A2 shows how these parameters have been calculated. The induction period was calculated considering the first and second derivate of the $\omega = f(t)$ function. The $\omega = f(t)$ curve can be divided in three regions. First a fast oxidation of the mangano-wustite to spinel happens; second, the induction period, characterized by the completion of oxidation to spinel and beginning of spinel oxidation to bixbyite; and third, the oxidation of spinel to bixbyite.

During the second stage, the induction period of the spinel oxidation to bixbyite is happening at the same time that some mangano-wüstite is finishing oxidizing to spinel. The method used to calculate the initial time for the induction period includes the determination of a line tangent to the $\omega = f(t)$ function at the time at which the second derivate $d^2\omega/dt^2$ present a minimum during the first stage; see Fig. A2. This tangent line is described by the following equation:

$$(y-0.964) = 3.30 \cdot 10^{-4} \cdot (x-50.3) \quad (A1)$$

Also, it is determined the line tangent to the $\omega = f(t)$ function where the first derivate $d\omega/dt$ presents a minimum during the second stage:

$$(y-0.971) = 4.87 \cdot 10^{-6} \cdot (x-178.2) \quad (A2)$$

The intersection between equations (A1) and (A2) determines the initial time for the induction period, which for the example shown in Fig. A2 is 71 s.

To determine the ending time of the induction period, it is calculated the line tangent to the $\omega = f(t)$ function at the point in which the first derivate $d\omega/dt$ present a maximum:

$$(y-0.982) = 6.10 \cdot 10^{-5} \cdot (x-537.5) \quad (A3)$$

The intersection between equations (A2) and (A3) determines the initial time for the induction period, which for the example shown in Fig. A2 is 373 s.

Therefore, the calculated induction period is $\tau_{ind} = 373 - 71 = 302$ s.

The spinel oxidation rate, $r_{ox}^{sp \rightarrow bix}$, was determined from the slope of equation (A3).

Fig. A1. (a)-(i): Evolution of the mass-based conversion vs. time as a function of the temperature and the partial pressure of O_2 observed for the 5th oxidation half-cycle.

Fig. A2. Evolution of the mass-based conversion vs. time for the 5th oxidation half-cycle of Mn₆₆FeTi₇ at 1148 K and supplying O₂ concentration of 10 vol%.

A.2. Determination of magnetic susceptibility.

A Bartington Instruments MS3 apparatus was used to measure the dimensionless volumetric magnetic susceptibility of a sample of solids putted in a small (1 cm³) container. The measured magnetic susceptibility, $\chi_{v,meass}$, depended on the amount of sample put inside the container, which depends on the porosity of both the packed bed and the particles. The mass-based relative magnetic susceptibility, $\chi_{m,r}$, is calculated by dividing the volumetric magnetic susceptibility, in the International System Units, by the density of the solid in the container, ρ_{bed} :

$$\chi_{m,r} = \frac{\chi_{v,meass}}{\rho_{bed}} \quad (A4)$$

Then, the relative volumetric magnetic susceptibility of the solid, $\chi_{v,r}$, is calculated considering the skeletal density of the particles, ρ_{solid} , measured by He-picnometry:

$$\chi_{v,r} = \chi_{m,r} \rho_{solid} \quad (A5)$$

In previous works [35,36], the relative magnetic permeability, μ_r , was calculated as:

$$\mu_r = \chi_{v,r} + 1 \quad (A6)$$

In the Table A.1, the values of μ_r and $\chi_{m,r}$ are compared for different materials previously tested.

Table A1. Magnetic properties of different materials.

Oxygen carrier	T _{calcination} [K]	ρ_{bed} [kg m ⁻³]	ρ_{solid} [kg m ⁻³]	$\chi_{v,meass}$ [-]	$\chi_{m,r}$ [m ³ kg ⁻¹]	μ_r [-]	Ref.
Mn77Fe	1223	866	5007	0.001	$9.9 \cdot 10^{-7}$	1.0	[35]
	1373	1134	4898	0.004	$3.5 \cdot 10^{-6}$	1.0	[35]
	1473	1306	5002	0.012	$8.9 \cdot 10^{-6}$	1.0	[35]
	1523	481	5005	0.165	$3.4 \cdot 10^{-4}$	2.7	[35]
	1623	1610	5010	0.495	$3.1 \cdot 10^{-4}$	2.5	[35]
FeTi7	1473	1618	4926	0.004	$2.5 \cdot 10^{-6}$	1.0	[36]
Mn28FeTi7	1473	1655	4815	1.653	$1.0 \cdot 10^{-3}$	5.8	[36]

Mn55FeTi7	1473	1726	4635	2.727	$1.6 \cdot 10^{-3}$	8.3	[36]
Mn66FeTi7	1473	1720	4692	2.511	$1.5 \cdot 10^{-3}$	7.8	[36]
Mn87FeTi7	1473	1770	4635	0.006	$3.4 \cdot 10^{-6}$	1.0	[36]
	1573	1781	4700	0.066	$3.7 \cdot 10^{-5}$	1.2	[36]
	1623	1792	4565	0.070	$3.9 \cdot 10^{-5}$	1.2	[36]
	1673	1795	4666	0.094	$5.2 \cdot 10^{-5}$	1.2	[36]
MnTi7	1473	1681	4707	0.006	$3.6 \cdot 10^{-6}$	1.0	[36]
	1673	950	4685	0.002	$2.1 \cdot 10^{-6}$	1.0	[36]
Mn66FeTi7	1223	866	4625	0.001	$9.1 \cdot 10^{-7}$	1.0	[this work]
	1323	846	4628	0.001	$9.2 \cdot 10^{-7}$	1.0	
	1373	1614	4630	0.097	$6.0 \cdot 10^{-5}$	1.3	
	1473	1651	4632	0.227	$1.4 \cdot 10^{-4}$	1.6	