



Article Extremely Stable and Durable Mixed Fe–Mn Oxides Supported on ZrO₂ for Practical Utilization in CLOU and CLC Processes

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Abstract: This paper contains the results of research on a promising combustion technology known as chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU). The remarkable advantages of CLC are, among others, that concentrated CO₂ stream can be obtained after water condensation without any energy penalty for its separation or significant decrease of NO_x emissions. The objective of this work was to prepare a novel bi-metallic Fe–Mn supported on ZrO₂ oxygen carriers. Performance of these carriers for the CLOU and CLC process with nitrogen/air and hard coal/air was evaluated. One-cycle CLC tests were conducted with supported Fe–Mn oxygen carriers in thermogravimetric analyzer utilizing hard coal as a fuel. The effects of the oxygen carrier chemical composition and process temperature on the reaction rates were determined. Our study proved that for CLOU, properties formation of bixbyite and spinel forms are responsible. Among iron ferrites, we concluded that iron-rich compounds such as Fe₂MnO₄ over FeMn₂O₄ spinel type oxides are more effective for CLOU applications.

Keywords: iron-manganese; mixed metal oxygen carrier; CLOU; CLC

1. Introduction

Due to increased demand on electrical energy combined with the necessity of the reduction of greenhouse gases emissions, new energy production methods need to be developed. Despite withdrawing from combustion of fossil fuels, combustion power plants still will have a considerable share in global energy production in the foreseeable future [1].

CLC (chemical looping combustion) is a new, promising technology for fuel combustion that allows to burn a wide range of fuels such as: gaseous (e.g., hydrogen, methane, syngas), liquid (hydrocarbons including heavy oils), and solid (coal, biomass) with significantly reduced emissions of pollutants as carbon dioxide or nitrogen oxides [1–3].

In the CLC process, a system of two reactors is used. In the first reactor, a material called oxygen carrier (OC) is oxidized at a high temperature by a stream of atmospheric air, and is then transported into the second (fuel) reactor where it is used to oxidize fuel. Oxidation of fuel may take place due to: (1) the releasing of gaseous oxygen from OC, in so-called CLOU—chemical looping with oxygen uncoupling; (2) due to direct reaction between OC and fuel, in so called CLC—chemical looping combustion; or (3) as a result of reaction of gaseous products coming from preliminary gasification of solid fuel particles and OC (ig-CLC—chemical looping combustion with in-situ gasification) [4]. Since fuel in the CLC process is separated from atmospheric air, this is the reason for restricting the production of nitrogen oxides which are usually formed during the conventional combustion process. Assuming that the combustion process occurs only in the presence of oxygen, similar to combusting fuels in pure oxygen (Oxy-combustion), the final products from the fuel reactor will be both carbon dioxide and steam. Furthermore, after water condensation, carbon dioxide could be removed in the carbon capture and storage process (CCS) or even reuse in carbon capture and utilization process (CCU) [1]. In comparison to



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Oxy-combustion, the main advantage of CLC is that there is no need to use an expensive air separation unit (ASU) [5].

As was stated before, the main function in the processes takes charge of the oxygen carrier. Materials used as OCs should show certain properties such as significantly high oxygen transport capacity, ability to maintain redox properties during multiply of working cycles and adequate mechanical strength to provide acceptable resistance for fragmentation in conditions that occur in fluidized bed reactors. Moreover, economically efficient OC should be formed from possibly cheap resources and should also be environmentally friendly. Many materials were recently under consideration as suitable candidates for OCs, including natural ores (e.g., ilmenite, iron ores etc.) [6] or synthetic materials purposely designated for that role as OCs based on mixed oxides, or perovskite-based OCs [7,8]. As a result of advanced study, various transitional metals oxides were examined as potential candidates for OCs such as copper, nickel, iron, manganese, or cobalt oxides. All of them have some advantages and disadvantages. Copper oxide, despite its promising oxygen transport capability, is fairly pricey and is also characterized by low melting point in comparison to other oxides. Nickel and cobalt show toxicity for both humans and the environment. Meanwhile iron oxides, despite their low price and environmental safety, do not exhibit desirable CLOU properties. They are also tending to agglomeration when reacted in high temperatures [4,9–11].

Oxygen carriers based on iron and manganese oxides are promising materials for that role [12]. In comparison to pure iron oxide, mixed Fe–Mn are experiencing CLOU capabilities and also have higher oxygen transport capacity, as was reported previously [13,14]. Similarly, they are relatively resistant to sulphur poisoning, which opens up an opportunity for using them for combustion of a wide range of fuels, such as coal, biomass, or biogas etc. [2,4,13–16]. Although in theory OCs based on pure Mn oxides should have decent capacity of oxygen transport, in practice they is exhibit poor CLOU capabilities due to the high equilibrium partial pressure of O_2 in the temperature range in which the fuel combustion process occurs (above 800 °C) [12,13,17]. Furthermore, they are also known for its poor oxidation characteristics during the regeneration stage. Additionally, it shows poor reactivity with methane and coal [2].

Meanwhile, CLOU properties of OCs are considerable important for the combustion of solid fuels. It has been experimentally demonstrated that combustion of coals occurs 3 to even 15 times faster (for low volatile petroleum coke) when OC exhibits those properties [13,18]. Mixing manganese oxides with other transitional metal oxides could enhance desired CLOU characteristics. It may occur due to the formation of (Fe,Mn)O₃ bixbyite phase, which is later reduced into the spinel phase of (Fe,Mn)O₄ in a low oxygen partial pressure environment. It was proved that a formation of rich manganese spinel forms could have a negative impact on regeneration of Fe–Mn OCs [13,19]. From the other hand, the occurrence of spinel phase may have some positive effect on the mechanical durability of Fe–Mn OCs as it has been reported in [16].

Published papers recently showed that some pure Fe–Mn oxides were already tested as OCs for fuel combustion in fluidized bed reactors. However, these were characterized by poor durability. During tests in circulating fluidized bed reactors, Ryden et al. reported bringing to an end the reaction due to OCs particle breakdown after 4 h of continuous work [17]. For further development those classes of OCs, an amplification of their mechanical strength is necessary. This could be achieved by using inert oxides as a support material. SiO₂, TiO₂, sepiolite, bentonite, Al₂O₃, or ZrO₂ are recently commonly used supports. ZrO₂ is a promising material to use as an inert since it usually does not react with the active phases of OC. It has been experimentally proved that Fe–Mn oxides system may be doped with 20% mas. of ZrO₂, with achieving a better performance during the combustion of synthesis gas than the systems based on other inerts such as sepiolite or Al₂O₃. Moreover, a strong positive temperature effect on the reduction rate of OC was reported [20]. The main drawback of ZrO₂ utilization is relatively higher unit cost than for other support materials.

The Aim

The purpose of this work is the examination of CLOU properties of mixed ironmanganese oxides and check their capacity for combustion of solid fuels. OCs based on Fe–Mn oxides due to the low cost, high oxygen transport capacity, and environmental safety are promising materials for CLC [12]. Additionally, supporting those materials with ZrO₂ have a positive effect on its mechanical strength. The parameter is important for the application of OCs materials in industrial scale CLC plant, and may be tailored by increasing the lifespan of OC [4]. Also, ZrO₂ as an inert material does not negative effect on the reactivity of Fe–Mn based materials [14,20]. As was stated earlier [13,18], OCs that exhibit CLOU properties show better performance during reaction with coal. Fe–Mn OCs were successfully tested as an effective and promising materials for hydrogen combustion, which was reported in paper [14].

While pure Fe–Mn mixed oxides or Fe–Mn spinel OCs were reported as having promising CLOU properties, zirconia supported Fe–Mn oxides have not yet been tested as materials for solid fuel combustion. In this work, CLOU properties of presented OCs were examined by thermogravimetric (TGA) method through temperature scanning up to 1200 °C with a heating rate of 5 K/min, to estimate the temperature range in which CLOU effect occurs, namely CLOU window. The TGA method was also used for examination of reduction/oxidation rates. While manganese addition may increase an oxygen transport capacity, formation of rich manganese spinel phases could have a negative impact on reaction kinetics and general reactivity of OC [13]. Thus, during the experiments the optimal composition was chosen for solid fuel combustion.

As a primary objective of the research was to obtain durable and efficient OCs, stability of samples was measured by X-ray powder diffraction (XRD), and any morphological changes were examined using scanning electron microscopy (SEM). Changes in crushing strength for both reacted and fresh samples were examined. As a fuel for combustion tests, hard coal (Janina) from Polish coal mine was selected. Fe–Mn based OCs, as fairly resistant for sulphur poisoning, are a suitable choice for hard coal combustion in CLC process [4,21]. Experiments were performed on TGA, serving as fixed bed reactor, coupled with a quadrupole mass spectrometer to analyse combustion gasses. Combustion tests were performed in 900, 950, and 1000 °C as those temperatures correspond well to the range of temperatures commonly used in CLC reactors.

The objective of this work was to prepare lower cost oxygen carriers from Fe–Mn and Zr oxides and examine their application for oxygen transfer in chemical looping with oxygen uncoupling and chemical looping coal combustion. In this work, OCs were tested for both gaseous (nitrogen) and solid fuel combustion (direct combustion of hard coal).

2. Results

2.1. Phase Composition, Mechanical Strength

In Figure 1, XRD patterns obtained for the five oxygen carriers for the family of Fe– Mn–Zr–O are shown. X-ray powder diffraction examination indicated that the obtained oxide samples were well crystalline ceramics (Figure 1). The crystal phases detected were mostly composed of Fe_2O_3 (between 37 and 55%), of varying amounts of bixbyite-type oxides (between 25 and 43%) with a general (Mn,Fe)₂O₃ formula, and finally of ZrO₂ (about 20%) for F65M15 to F50M30 ceramics. For so-called reference material (not containing Mn addition), i.e., F80 sample, both Fe_2O_3 and ZrO₂ were detected.

Since different OCs reactivity tests were performed, phase identification was likewise carried out for the reacted samples. As a consequence, in Figure 1, X-ray powder diffraction patterns recorded for both unreacted and reacted with coal samples at different temperatures were enclosed. The results will be further discussed and compared when describing the regeneration stage of OCs.



Figure 1. Comparison of X-ray powder diffraction patterns between fresh and reacted with coal OCs samples.

Mechanical strength, as one of the most important process parameters, reflecting the functional properties of the prepared samples, is just as crucial as the reactivity of oxygen carriers or the ability to transfer oxygen. Depending on the resistance of the grains to compressive and abrasive forces, their ability to be reused in the reduction process with fuel may be assessed. Samples showing low mechanical strength will quickly deteriorate, which leads to the necessity to replace them with new ones to continue the process. This treatment is unfavourable from the economic point of view, generating additional costs (even with low costs of the synthesis of oxygen carriers) if the process is used for industrial purposes. Crushing strength is a simple measure and may give a valuable first indication of whether a particle has sufficient strength or not. Crushing strength below a certain threshold leads to easy particle breakage, which is unfavorable for CLC. A rule of thumb is that materials with a crushing strength less than 1N will not perform well in fluidized beds. Other sources report that particles with a crushing strength above 2N were more likely to perform well, compared with softer particles during continuous operation at an elevated temperature in fluidized beds, since they had a high attrition resistance [22,23].

For this reason, the crushing strength analysis was performed to evaluate the strength and durability of the synthesized Fe-Mn-Zr-O based OCs. Figure 2 shows the measured values of the mechanical strength for the five analyzed samples, prepared in accordance with the described synthesis conditions. Additionally, the F50M30 T1050 sample, for comparison purposes, was prepared. This sample was calcined at higher temperature, i.e., 1050 °C during 11 h. Figure 2 also shows the measured strength for the spent OCs materials. These data will be analyzed further in detail when discussing the regeneration ability of obtained solid state OCs. The results showed without doubt that the fresh F50M30 sample calcined at 950 °C has the highest average strength, while the same composition sample F50M30 T1050 calcined at 1050 °C sample has achieved the lowest value. Previously, some influence of temperature during synthesis of oxygen carriers was shown in the literature [24], where the F50M30 sample was calcined at 850 °C and 1050 °C. The results of the mechanical strength tests obtained in this work confirm the good direction of calcination temperature selection for oxygen carriers based on Fe-Mn/Zr oxides. The average values of the mechanical strength are characterized by an upward trend with an increase of manganese dioxide content in the sample and with a decrease in calcination temperature. The average values of the mechanical strength for individual samples are as follows: F50M30 T1050 (0.47 N) < F80 (0.55 N) < F65M15 (0.78 N) < F60M20 (0.83 N), F55M25 (0.88 N), and finally F50M30 (0.95 N). According to the literature data, the analysed material (Fe_{0.25}Mn_{0.75})₂O₃/ZrO₂, calcined at three different temperatures: 950, 1100, and 1200 °C, was characterized by a strength of 0.7, 0.6, and 0.5 N, respectively. This means that in our work the selected mass compositions of the oxides and simultaneously the use of a lower calcination temperature improved the strength of the materials compared to the data presented in the literature. The obtained results are satisfactory. Figure 2 also shows that for the compositions of F50M30, F55M25 there are grains with strength values approximately 1–1.5 N. This may indicate the formation of compounds rich in manganese, which are especially durable. Results of crushing strength testing indicated that the developed materials had a pronounced mechanical resistivity, and compared to the literature data, an improvement of mechanical strength is clear.



Figure 2. Mechanical strength test results for as-synthesized and for spent Fe-Mn/ZrO₂ family oxygen carriers.

2.2. CLOU Window and CLOU Properties of Featured Samples

Since OC materials with a chemical looping, oxygen uncoupling (CLOU) effect may give additional benefits to those of CLC due to faster fuel combustion and gasification for this reason, this is evaluated in the paper. First, the samples were pre-calcined in flowing air in 1200 °C to ensure they are in the oxidized form and to remove possible humidity. The main part of the study was to re-oxidise metal oxide samples by air (21% O_2/N_2) during cooling to room temperature, and continuing experiment by reducing the samples by heating to 1200 °C in inert conditions (100% N_2) to determine possible CLOU effect. CLOU window examination is shown in Figure 3.

All mixed metal Fe–Mn oxides show increase in mass during oxidation when cooling down. While the reference material monometallic Zr supported Fe did not show any mass change, as it is expected (not shown), meaning a lack of CLOU properties.

For samples with the lowest Mn addition (i.e., F65M15), the release of oxygen is detected ca. 800 °C. When heating further in an inert atmosphere, a small weight loss of 0.15 wt.% at 1000 °C, and clear weight loss was detected at 1200 °C of 1.45 wt.% indicated a possible CLOU effect. For the F60M20 composition, the CLOU effect is increasing from 0.2 to 1.2 wt.% between 900 and 1200 °C, while for F55M25 it is 0.3–0.9 wt.%, respectively. The heating under an inert atmosphere leads F50M30 to evolving of oxygen amounted to 0.3–0.7 wt.%. For all bimetallic samples a two-step reduction is detected indicating possible dual phase presence. In our previous paper, indeed, FactSage thermodynamic calculations likely showed the presence of manganoferrite and manganowüstite.

In paper [12], pure Fe:Mn oxides without support were obtained. In this work additionally Zr oxide supported OCs were obtained with an estimated ratio of Fe:Mn oxides ca. 4.5:1 for F65M15 to 1.7:1 F50M30. For previously reported F5M1 composition, the CLOU effect ca. 0.5–2% between 900 and 1150 °C, and for F2M1 0.3–0.5% was observed. Comparison shows that for F65M15 sample with 1.7:1 ratio (this paper) and F2M1 2:1 (reported previously) [12] better CLOU effect was achieved by application of inert addition. Beneficial additions may lead to profound increase of CLOU value from 0.5 to 1.45%. Nevertheless, for higher Fe:Mn oxides ratio the possible CLOU effects above 900 °C were of similar values both for supported and unsupported OCs materials. The trends found here are also in agreement with published data [12].



Figure 3. Mass change in temperature screening experiment (oxide samples are reoxidised by cooling in $21\% O_2/N_2$ and then reduced by heating in 100% N₂).

To evaluate reductions in an inert atmosphere and oxidations in function of chemical composition of the produced materials together with the estimation effect of temperature, multiply cycles were carried out. The reactivity experiments were carried out at 800–1100 °C temperature range with a 50 °C step in TGA using N₂ and O₂/N₂ for reduction

and OCs material regeneration, respectively. At each temperature, three redox cycles were applied to estimate the stability of the carriers.

Oxygen transport capacity versus chemical composition of iron-manganese-zirconia oxide-based OCs is shown in Figure 4a, while the capacity in function of temperature is shown in Figure 4b. The presented data are taken from the second TG cycle. Oxygen transport capacity for the iron-manganese-zirconia oxide-based system (Figure 4b) indicates in the lower temperature range (800–900 °C) that the experimental capacity increases with an increase of manganese content in the sample. Then, it drops at 950 °C to ca. 0.5 wt.% for all samples, and from this point it reverses. In other words, samples with lower amount of manganese content show better oxygen capacity. This will be explained later in detail. Cycling experiments allow us to study the capacity over several cycles and also to validate whether the fully oxidized or reduced states can be recovered after several redox reactions.



Figure 4. Oxygen transport capacity versus chemical composition (**a**) of iron-manganese-zirconia oxide-based OCs and reaction temperature (**b**).

The reaction rates (dX/dt) were calculated by differentiating the mass data versus time and they mean the rates at the maximum of DTG peak. The calculated reaction rates are shown for both reduction and regeneration reactions of OC materials in Figure 5. The metal oxide reduction rates slightly increase with temperature, and reaching ca. 0.5%/min at 1100 °C. They are of reasonable value, and more importantly are not as quick.

The temperature positively influences the oxidation rate for all OCs. One should also note that the regeneration reactions are much faster than reductions. It has a practical importance. Moderate rate of the oxygen loss observed when the oxygen partial pressure decreases may be beneficial in CLC process if the capacity is properly transferred to the fuel reactor. In other case it might be lost during transferring to fuel reactor, for example in loop seal etc. From the other hand, fast oxidation rates enable beneficial shortening of residence time in an air reactor. For this reason, in the work applied OC's moderate manganese content (15–30 wt.%) may lead to conclusion to have a high potential as CLOU materials in CLC processes.



Figure 5. Redox reaction rates in function of temperature for Fe₂O₃-MnO₂/ZrO₂ family.

Stability of work during CLOU processes is shown in Figure 6. It is clear to see that all synthesized OCs materials show stable reactivity within cycle number and temperature. At this point diverse behavior then expected shown in Figure 4, together with Figure 5 may be explained. The decrease of CLOU effect at 950 $^{\circ}$ C, together with the drop the oxidation

rate at 900 °C may be due to phase transformation. To explain that phenomenon additional work was carried out. Based on FactSage thermodynamic calculations, it was predicted that spinel will be formed instead of bixbyite when the partial pressure of O_2 will decrease, together with increase of temperature [13,14]. To prove possible negative impact of some spinel formation on oxygen carrier reactivity, which was reported previously [11,17], two different Fe:Mn spinels with ratio of 1:2 and 2:1 were additionally synthesized. Those two members of the manganese ferrite family were synthesized from high-quality powdered oxides and calcined in in 1050 °C for 6h in a furnace. The spinel structure of iron (Fe₂MnO₄), and manganese-rich (FeMn₂O₄) samples was confirmed by XRD tests. The oxides were subjected to analogical testing of reactivity in TGA. Results of those examinations are shown in Figure 7. Fe₂MnO₄ worked fine during CLOU testing, with a profound increase of capacity with maximum in 900 °C ca 2 wt.%. Dependent upon temperature, a significantly different behavior is observed for FeMn₂O₄ samples. Some CLOU effect (ca. 0.5 wt.%) is observed in the beginning of cycling in lower temperatures, but it disappears when testing above 850 °C.



Figure 6. Stable CLOU performance during cycling TGA test.



Figure 7. Cyclic TGA results for Fe₂MnO₄ and FeMn₂O₄ spinel type oxides.

High manganese content spinel was initially partially reactive, and followed by poorly activity during CLOU tests. This may be an explanation of the minor than expected CLOU behavior in higher temperature range for bimetallic Fe-Mn/Zr OCs materials with 20 and 30 wt.% of MnO₂. While the activity and weight gain of low manganese i.e., manganese diiron oxide, Fe₂MnO₄ observed in Figure 8 might be an explanation of CLOU behavior of OCs with 10 and 15% addition. Better than expected experimentally proved redox rates together with the superior amount of oxygen released may be a consequence of the Fe₂MnO₄ presence, which was proved by EDS. Later manganese ferrite, observed in OCs reduced samples, was satisfactory oxidized back to bixbyite form.

As a result of difference of CLOU activity between spinel forms, either rich in Mn or in Fe may be an explanation of "s" shape of the curve for oxygen transportation shown in Figure 4b, which is observed as increase and decrease of oxygen capacity. The further increase of capacities could be explained by of transition from spinel Mn-rich phase to manganowuestite, when heating from 950 °C up to 1100 °C. Therefore, the increase in oxygen capacity value is due to further deeper reduction of oxide spinel forms to $Mn_xFe_{1-x}O$, which was proved by FactSage calculations [12,14].



Among iron ferrites, we conclude that iron-rich such as Fe₂MnO₄ over FeMn₂O₄ spinel type oxides are more effective for CLOU applications.

Figure 8. Coal combustion with oxygen released from structure of Fe-Mn/Zr OCs at 900 °C.

2.3. CLC and CLOU Reaction Performance of Mixed Metal Fe-Mn/ZrO₂ Oxygen Carriers Using Hard Coal

Direct coal combustion is an option in CLC and CLOU processes. In our study, for this reason one-cycle TGA reduction of OC followed by its oxidation tests were performed. At high temperatures, the direct combustion of metal oxide and carbon is thermodynamically favored. The results of the thermogravimetric analysis of the Janina coal combustion at 900 °C with oxygen released from the structures of both bi-metallic Fe–Mn and mono-metallic supported Fe OCs are shown in Figure 8. The metal oxide:coal mixtures were prepared as discussed in the Synthesis and Materials Quality Examination section. One reduction/oxidation cycle tests were conducted at atmospheric pressure to determine the reactivity of the oxygen carriers. In this study, the one-cycle test was chosen, since from a technical point of view, in TGA, it is difficult to separate coal ash from metal oxide after redox reaction and continue cycling with a new coal portion. In real CLC systems, there are known technical approaches of removing the coal ash from OC that are based, for example

on density differences. Additionally, the one-cycle redox test provides all the needed data on the reactivity of OC.

Figure 8 shows both the mass changes versus time and calculated reaction rates. The black line illustrates changes in mass, wt.%, for both the bi-metallic oxygen carriers, i.e., F65M15-F50M30, and for mono-metallic F80 counterpart, whereas the blue line illustrates the changes in the calculated reaction rates, %/min. It should be pointed out that the heating rate was 15 K/min, and the desired temperature of the process was achieved in nearly 60 min. The measurement was then performed isothermally, which reflects the temperature curve. A steady mass loss of coal: oxygen carrier mixture was observed in approximately 175 min. The included results of the reactivity study at 900 °C exhibited that all obtained oxygen carriers reacted with hard coal. This is indicated by a mass decrease observed within the reaction time.

The aim was also to study the impact of chemical composition of OC on coal combustion. For this reason, both new bimetallic Fe–Mn oxides were synthesized and monometallic. Monometallic OC, also called simple OC, includes usually one active oxide, here in the form of iron oxide and one inert material. Among simple OC, we included both iron oxide and manganese oxide (actively participating in the redox reaction), as well as one inert oxide, here ZrO₂.

The TG data (Figure 8) clearly displayed gradual mass decrease. They can be number 1, 2, and 3 and 4. The maximal reaction rates observed at given temperatures during the reduction and oxidation reactions of oxygen carriers with hard coal are listed in Table 1 Steps number 1 corresponded to a hard coal volatilization reaction that was initiated at ca. 400 °C and for which the maximum reaction rate occurred at the range between 437 and 439 °C. In general, the coal pyrolysis temperature does not depend on the oxygen carrier composition which was also previously observed for other bimetallic OCs [25]. QMS signals of CH₄, H₂, CO, and CO₂ confirmed that the hard coal pyrolysis took place at this stage, Figure 9. Before coal volatilization a small peak originating from humidity was also observed (blue line QMS signal) with maximum detected at 7 min from begin of the experiment.



Figure 9. QMS data collected during the direct combustion experiment for mixture Janina coal: Fe50Mn30/Zr OC at 900 $^{\circ}$ C.

Sample	F50M30						
Combustion temp. (°C)	900		950		1000		
Peak No	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	
1	0.170	438	0.164	439	0.168	439	
2	0.179	633	0.177	633	0.177	633	
3	0.384	900	1.012	948	1.290	962	
Regeneration	1.321	900	1.720	950	2.166	1000	
Sample	F55M25						
Combustion temp. (°C)	900		950		1000		
Peak No	Reaction rate (%/min)	Temp.(°C)	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	
1	0.169	439	0.164	439	0.178	439	
2	0.182	640	0.179	640	0.189	640	
3	0.377	900	1.016	900	1.274	962	
Regeneration	1.386	900	1.386	900	2.146	1000	
Sample	F60M20						
Combustion	90	0	050		1000		
Temp. (°C)	900		900		1000		
Peak No	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	
1	0.164	439	0.163	439	0.172	439	
2	0.202	633	0.205	633	0.213	633	
3	0.348	900	0.991	948	1.291	963	
Regeneration	1.370	900	1.879	950	2.194	1000	
Sample			F65N	A15			
Combustion temp. (°C)	900		950		1000		
Peak No	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	
1	0.169	437	0.171	439	0.170	439	
2	0.179	633	0.209	633	0.213	633	
3	0.383	900	1.010	948	1.288	963	
Regeneration	1.321	900	1.946	950	2.146	950	
Sample	F80						
Combustion temp. (°C)	900		950		1000		
Peak No	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	Reaction rate (%/min)	Temp. (°C)	
1	0.166	439	0.165	439	0.169	439	
2	0.213	640	0.220	633	0.227	633	
3	0.151	798	0.207	866	0.207	843	
4	0.260	900	0.968	950	1.324	970	
Regeneration	1.287	900	1.989	950	2.208	1000	

Table 1. Maximal reaction rates observed during the reduction and oxidation reactions of oxygen carriers for process examined at 900, 950, and 1000 $^{\circ}$ C.

Steps 2, 3, and 4 correspond to the coal combustion reaction, which was initiated at approximately 600 °C, in general. This was also supported by quadrupole mass spectrometer data shown for example for Fe50Mn30/Zr sample in Figure 9. As combustion process proceed in TGA chamber the evidence of CO₂ (grey line) and H₂O (blue line) signal was

continuously monitored. Already at 37 min of the experiment and at 588 °C temperature, combustion was proved for the sample and meanwhile broad peak for H_2O was observed, while for CO_2 two separate signals were found.

Steps 2 and 3 were observed for bimetallic oxygen carriers. The mixture of coal with bi-metallic Fe-Mn/ZrO₂ oxides show only two mass decreases. Additional peak No 4 was only observed for F80 sample. This additional peak could be explained by the release of oxide from the Fe_2O_3 oxide which is due to step reduction to Fe_3O_4 , FeO and finally to Fe. This behavior was also previously observed for other monometallic Fe-based OCs such for 80 wt.% Fe_2O_3/SiO_2 , 80 wt.% Fe_2O_3 /sepiolite or 80 wt.% Fe_2O_3 /bentonite [25]. As shown in Figure 8, a systematic decrease in the mass mixture of coal:oxygen carrier was observed. Peaks with the highest reaction rates in the range of 633–900 °C reflect the first partial, afterwards complete fuel combustion. The partial reduction of the oxygen carrier from Fe_2O_3 to Fe_3O_4 /FeO together with bixbyite of $(Mn,Fe)_2O_3$ to spinel form of general Mn_xFe_vO₄. This is may be explained due to phase composition obtained OCs where dominant reactive phases were both Fe₂O₃ (ca. 37–55%) and (Mn,Fe)₂O₃ (ca. 24– 43%). Here, the reduction may process via manganese or iron reached cubic or tetragonal spinels such as iwakiite. The peak observed maximum detected at 798 °C reflects the reduction of the OCs part from Fe_3O_4/FeO to Fe/FeO. The data from Table 1 indicates hard coal combustion may occur as low as at 633 °C with a maximum rate of 0.179 to 0.213%/min. Afterwards, at 900 $^\circ$ C mass decrease peaks with a maximum rate between 0.260 and 0.384%/min are observed. All samples containing MnO₂ showed improved reactivity due to rate enhanced by the factor of 1.34–1.47. Therefore, a conclusion may be drawn, due to addition of 15–30 wt.% manganese oxide to Fe_2O_3/ZrO_2 improved reactivity of OCs carrier in direct coal chemical looping combustion may be achieved comparing to simple monometallic OC.

In addition to the impact of chemical composition of OC, the temperature effect of coal combustion was also examined in detail. For this reason, the study examined the reactivity of Fe-Mn/Zr OC by using combined methods such TGA and QMS in a similar manner as described for 900 °C temperature.

As a result, 950 °C and 1000 °C temperatures were selected for further examinations. Figure 10 shows results for coal combustion with oxygen released from structure of Fe-Mn/Zr OCs at 950 °C, while Figure 11 shows for 1000 °C. Additionally, maximal reaction rates observed during redox reactions of OCs for process examined at 950 °C and 1000 °C are shown in Table 1.

Besides, Figures 10 and 11 together with the detailed data from Table 1 illustrate well the positive effect of temperature on hard coal combustion via direct chemical looping. Only 50 °C decrease in process temperature led to significant improvement of reaction rates. For example, for the sample with the highest addition of manganese oxide (i.e., for F50M30 rate increased from 0.384 to 1.012%/min at 950 °C). Furthermore, the experiments carried out at 1000 °C showed an additional combustion rate increase to 1.290%/min. That is clear that between 900 and 1000 °C the OCs reductions rate increased significantly, which is estimated at over three times. This may have a practical meaning in CLC plants enabling significantly reducing the residence time.

2.4. Regeneration Reaction Performance of Mixed Metal Fe-Mn/ZrO₂ Oxygen Carriers Following Hard Coal Combustion

The reactivity study observations through TG for both redox reactions demonstrated that a process of pyrolysis is followed by the combustion of the fuel with oxygen released from the structure of OC. This has been observed for all obtained materials.

Aside from good reactivity with fuel, also good reactivity with air was observed in the TG curves, which is illustrated well in Figures 8, 10 and 11. This means bimetallic Fe-Mn/Zr OCs could be satisfyingly oxidized in the applied reaction conditions.

Additionally, the regeneration reaction rates were significantly faster than those observed for OCs reduction reaction which is observed by intensive and fast sample mass increase. For example, for F55M25 OC, at 900 $^{\circ}$ C reductions rates were 0.182 and 0.377%/min,

while oxidation rate was estimated at 1.386%/min. The oxidation reaction was significantly faster than the reduction reaction for all Zr supported Fe–Mn oxygen carriers. Furthermore, with increase of regeneration process temperature also the rates have increased. As for F55M25, OC regeneration rate further increased to 1.824 and 2.146%/min for 950, and 1000 °C, respectively.

The thermogravimetric results indicated that good reactivity was observed both for the bi-metallic and mono-metallic carriers. Due to the synergy effect of two reactive oxides (i.e., Fe_2O_3 and MnO_{2}), new crystal phases are formed such as $(Mn,Fe)_2O_3$ type. This is the reason improved oxidation could be achieved compared to pure MnO_2 oxide. This known that MnO_2 due to thermodynamic restrictions is difficult to oxidize to original form in higher temperatures. Consequently, the addition of a second reactive metal oxide stabilized the oxygen carrier structure, which enabled better reduction rates together with better oxidation rates to be achieved.



Figure 10. Coal combustion with oxygen released from structure of Fe-Mn/Zr OCs at 950 °C.

F50M30

25

50

75

100

Time (min)

125

100

Mass (%) 66

90

85





Figure 11. Coal combustion with oxygen released from structure of Fe-Mn/Zr OCs at 1000 °C.

Our experiments proved that O_2 content in air, in a TGA chamber acting as an air reactor, is sufficient to perform the oxidation up to the bixbyite and spinel phases. When the capacity (CLOU 0.5–1.5 wt.%, and CLC ca. 20 wt.%) is properly transferred to the fuel reactor, obtained in this work the family of Fe-Mn/Zr may have a high potential both as a CLOU and CLC material.

Figure 12 shows photomicrographs of F50M30 OC granules ($450 \times$ magnification) after reaction with Janina coal. This is worth to note that for reacted with hard coal samples and regenerated, some morphological differences are clear. In our previous paper we have observed that the fresh samples were very similar for Fe–Mn/ZrO₂ family [13,14]. However, here the reacted samples show some variety of forms. Some of the particles are regular in shape and more porous with fine sub-granular structure (Figure 12c,d). Other spent grains seem to be denser (Figure 12a,b) and slightly longitudinal. The spent F50M30 OC grains shown in Figure 12a,b with the assistance of EDS were proved to be tetragonal Mn–Fe spinel's with some zirconia spots, and tetragonal Mn–Fe spinel with bixbyite, respectively. While those porous grains were composed of iron oxides with some zirconia. As a consequence, OCs reacted with Janina coal and afterwards regenerated in flowing air exhibited also mechanical changes.



Figure 12. Morphological features of different F50M30 OC granules (a-d) after reaction with Janina coal in 900 °C.

Those morphology and crystal phase changes may be an explanation of better mechanical properties characteristics which is shown in Figure 2. The mechanical strength, in addition to the ability to transfer oxygen, is one of the most important process parameters studied in this paper. When describing the functional properties of the newly prepared OCs samples they must be considered. Depending on the resistance of the grains to compressive and abrasive forces, their ability to be recycled and reused in the reduction process with fuel can be estimated. For this purpose, in this work we analyzed the mechanical strength both for fresh and reacted samples. As observed from Figure 2, fresh bimetallic OCs showed measured average strength values ranging from 0.78 N for F65M15 to 0.95 N for F50M30, which positively increased with manganese addition to monometallic Fe-based OC. For the samples reacted with hard coal at 900 °C the mechanical tests revealed an increase in durability for ca. 60% comparing that observed for fresh samples. For example, for F50M30 average value was 1.5; 1.37; 1.2 N for 30 analyzed grains at 900, 950, and 1000 °C, while for F55M20 it was 1.3; 1.4; and 1.1 N, respectively. Despite being more resistant, reacted ceramics exhibited more diverse durability for mechanical crushing than unreacted samples (Figure 2). Furthermore, SEM analysis of individual OC particles revealed different morphological topographies were more likely associated with their individual composition (Figures 1 and 12).

Additionally, XRD analysis shown in Figure 1 for both fresh and reacted samples exhibited some differences in phase composition due to OC cycling performance, which supports SEM discoveries. Fresh samples contained (Fe,Mn)O₃ type, Fe₂O₃ and ZrO₂ oxides. Later the reaction with hard coal, the diffraction data revealed the presence of specific manganese-rich tetragonal spinel, so called iwakiite, i.e., (Fe_{1.3}Mn_{1.7})₂O₄, which is observed for manganese reached bimetallic material, F50M30. As process temperature increased from 900 to 1000 °C the amount of iwakiite manganoferrite increased (red, blue, and green diffractograms, respectively). Nevertheless, different behavior was observed for OC with 25–15 wt.% addition of manganese oxide. For the sample with 25 wt.% addition, i.e., F55M25 due to coal combustion executed at 900 °C, regenerated OC sample showed, aside of bixbyite and also Fe-rich cubic manganoferrite. Fe–Mn bixbyite structures can be usually present in multiply forms of (Fe_xMn_{1-x})₂O₃ with variable ratio of Fe:Mn. During

the fuel combustion process it was observed that specifically (Fe,Mn)O₃ structures were reduced and regenerated however, to manganoferrites. Our data proved that bixbyite structures can be regenerated partially revisable to original perovskite type structures in those TGA conditions. The obtained results are in contrast with published FactSage simulations [13,14]. From the other hand, they are in good agreement with other literature findings [13,14]. It has been observed during temperature-scanning experiments that the Fe:Mn samples could be reduced to spinel as the temperature increased, even under an oxidizing atmosphere.

As a consequence, spinel structures will be present in obtained materials. Based on this work, observations, among iron ferrites, iron-rich such as Fe_2MnO_4 over $FeMn_2O_4$ spinel type oxides are more effective for CLOU applications can be concluded. XRD data together with SEM-EDS supported that 25–10 wt.% addition of MnO_2 , together 20 wt.% addition of ZrO_2 may prevent undesirable $FeMn_2O_4$ formation (small and disappearing CLOU effect). At this point, the presence of well-shaped crystal structures observed in manganese-rich OC samples might be partially responsible for their durability. In general, the conclusion on valuable regeneration of Zr supported bimetallic Fe–Mn OCs can be withdrawn. This is supported by the observation of TGA results together with the obtained strength analysis data. It is clear that synthesized materials showed significantly improved mechanical strength.

3. Materials and Methods

3.1. Synthesis and Materials Quality Examination

Five samples of Fe₂O₃-MnO₂ family supported on 20 wt.% ZrO₂, were prepared by using the mechanical mixing method (Table 2). High quality powders of Fe₂O₃ and MnO₂ (<99%, Sigma Aldrich, St. Louis, MO, USA) were mixed roughly with ZrO₂, and deionized water was added to obtain a paste. The paste was dried, crushed, and calcined at 950 °C in air for 8 h. 10 wt.% of graphite was added to the mixture to improve the porosity of the prepared samples. The use of graphite addition was due to the fact that this is a well-known agent enabling increase of porosity, while it is oxidized to CO₂ during calcination at 950 °C in the air atmosphere. After cooling down, the procedure was repeated, the samples were crushed and carefully mixed with water and a new graphite portion. Next, the samples were calcined at 950 °C in air for 8 h. Finally, the desired fraction of 125–180 μ m was obtained after sieving. In the paper hereafter, the following denotes the mean. For example, F65M15 symbol refers to 65 wt.% Fe₂O₃-15 wt.% MnO₂ and 20 wt.% ZrO₂ samples, etc. As a result, five different oxygen carriers were obtained (Table 2). The procedure and temperature selected (950 °C) was based on our previous experience gained [14] and the knowledge on the possible phase transitions of ZrO₂ (ca. 1170 °C) that may occur.

Sample	Fe ₂ O ₃ (wt.%)	MnO ₂ (wt.%)	ZrO ₂ (wt.%)
F80	80	х	20
F65M15	65	15	20
F60M20	60	20	20
F55M25	55	25	20
F50M30	50	30	20

Table 2. The obtained OC samples	Table 2.	The obtained	OC samp	les.
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Hard coal from the Janina coal mine in Poland was selected for solid fuel CLOU and CLC examinations. The technical, ultimate and proximate analyses data were published elsewhere [25]. The particle size of the coal samples used in this study was <200 μ m. The Janina coal is known as a typical power coal which exhibits high reactivity. In this study, it was carefully chosen since it is a prospective coal for use in coal combustion and gasification in Poland. As indicated previously it's of high quality due to both high calorific value of ca. 25 MJ/kg, and low sulphur and ash contents, <1.5% and <7%, respectively. For

this reason, it was selected for chemical looping combustion and chemical looping with oxygen uncoupling tests.

Mechanical strength is one of the key parameters determining the functional properties of the obtained mixed compounds. It is desirable to have the highest possible value of the compressive and abrasive forces acting on the oxygen carrier grains during the thermal process. The greater the mechanical stress a granule can withstand and not be damaged at the same time, the more resistant it is (e.g., to abrasion). The mutual abrasion of granules of mixed compounds is an undesirable effect, especially when we want to use oxygen carriers as long as possible. Particle breaking testing was performed to evaluate the strength and durability of synthesized oxygen carriers. To study mechanical strength of Fe–Mn–Zr–O materials Digital Force Gauge Shimpo FG-5000A, by Shimpo Instruments, Japan model was used. The instrument provides solid force testing within a capacity of 5.0 kg and a resolution of 0.001 kg. For testing 30 particles of each composition of the OCs have been analyzed.

3.2. X-ray Powder Diffraction

XRD patterns of both as synthesized, namely "fresh" Fe₂O₃-MnO₂ oxygen carriers, and after reaction with nitrogen/air and coal/air namely "reacted" were collected at room temperature using the X-ray powder diffractometer MiniFlex600 by RIGAKU, Japan. The experiments were carried out at following conditions 40 kV, 15 mA, with a filtered CuK α radiation of $\lambda = 1.54056$ Å. The diffraction patterns were collected with a step of 0.02°, within the 2 θ range of 20–80°. The crystalline phase identification and quantification was performed with the application of ICSD data. The quantitative analysis was performed by using of The Reference Intensity Ratio (RIR) method.

3.3. Microstructure

The microstructure of the materials surface was studied using scanning electron microscopy, by means of the JEOL JSM—6610 LV, Japan instrument with an energy dispersion X-ray spectrometer for chemical microanalysis purposes. The surface morphology was studied by gluing carbon tape onto the samples. Carbon tape was not used in the chemical analysis of the samples. The study was conducted using a low vacuum detector at an accelerating voltage of 15 kV and different magnification of images $100-1500 \times$. The EDS Oxford Aztec Energy, Japan with an Si(Li) X-ray detector was used for investigation of the homogeneity of the samples. The composition analysis by EDS was performed. During this study, an analysis of the composition of the entire grain surface was carried out (due to the presence of the elements: Fe, Mn, Zr, and O), and a linear analysis of selected grain fragments to examine the composition and possible presence of the expected structures.

3.4. Thermogravimetric Analysis (TG)

Thermogravimetric experiments were conducted using a thermal analyzer (STA 409 F5 Jupiter by Netzsch Selb, Germany) which was coupled to quadrupole mass spectrometer QMS 403 Aëolos Quadro (Netzsch Selb, Germany). The mass spectrometer used for the evolved gas analysis could detect mass numbers of 1–300 amu in the MID mode. In the experiments, the mass changes of the metal oxide OCs were measured isothermally as a function of time.

Three types of reactivity experiments were carried out with TG-QMS. The first of them is the CLOU window experiment followed by a modified experiment setup published elsewhere [12]. Ca. 10 mg OC sample was heated in a synthetic air atmosphere with a heating rate of 5 K/min, with a 75 mL/min flow rate. The sample was pretreated this way up to 1200 °C. When a temperature of 1200 °C was reached, the sample was slowly cooled down still in oxidizing conditions with a cooling rate of 5 K/min and 75 mL/min flow rate of synthetic air. As the sample reached room temperature, the next step was introducing N₂ with 75 mL/min flow rate, and increasing temperature up to 1200 °C with 5 K/min rate. Continuously mass changes were registered during the experiment. As the TG analyzer

cooled down, the samples were collected for post-experiment analysis (i.e., for determining possible morphology and crystal phase changes). The second type of reactivity experiments contained CLOU effect study within multiply cycles and temperatures. For that reason, ca. 10 mg dried sample was placed in the Al₂O₃ crucible. The sample was heated to desired temperature of 800 °C with 20 K/min rate, using N₂ gas rate of 100 mL/min. Then the sample was held for 5 min and flushed with synthetic air as a stabilization stage. Afterwards, the experiment was started with the consecutive introduction of reducing (N₂) and oxidizing gases (synthetic air). As a result, the oxygen carrier particles were exposed to three successive reduction-oxidation cycles, conducted at atmospheric pressure to determine the CLOU reactivity. CLOU stage endured 20 min with 100 mL/min of N₂, while the regeneration stage was set at 10 min with 100 mL/min of synthetic air (20% of oxygen balanced by nitrogen). To understand the effect of temperature. TGA experiments of CLOU were carried out at 800–1100 °C temperature range with 50 °C steps while reduction-oxidation cycles were conducted at atmospheric pressure to determine the stability of the carriers.

Prior to testing, additional experiments were carried out enabling experimental conditions to be set up. As a result, both the oxygen carrier mass and gas flow rates used in the TGA experiments were selected to avoid limitations in the external film mass transfer and interparticle diffusion.

Additionally, the OCs and the coal samples were dried at 115 °C to remove humidity before the thermogravimetric tests. The third type of reactivity experiments contained both CLC and CLOU effects study. In the baseline coal tests, approximately 200 mg sample was heated in a Al₂O₃ crucible with Ar purged to the desired temperature 900 °C (950 °C, or 1000 °C) at a heating rate of 15 K/min. In this type of experiment, broadly used in Poland, energy coal, namely Janina hard coal, was used for the reduction reaction, and synthetic air was used for the OC regeneration. To do so, Fe-Mn/Zr oxygen carrier materials were physically mixed with the coal. Based on calculations (oxygen carrier material theoretical oxygen capacity and physical-chemical characteristics of the hard coal), the oxygen carrier to ash free coal mass ratio was selected. This was an optimum 12.7:1 ratio to provide possibly full combustion of hard coal. The mixture of OC and coal was heated to the desired testing temperature for example 900 °C in TG. After the set temperature was reached, the isothermal measurement was performed for 120 min. While the regeneration stage of Fe-Mn/Zr OC was set up for 30 min with synthetic air flow rate of 80 mL/min. For comparison purposes, coal samples were measured individually in the TG under the same experimental conditions as for the mixtures.

During the TG experiments, the mass change of the metal oxide oxygen carriers was measured isothermally as a function of time. One reduction/oxidation cycle was conducted at atmospheric pressure to determine the reactivity of the oxygen carriers. To answer the question on temperature influence, the same experiments were repeated for 950 °C and 1000 °C.

The reaction rates (dX/dt) were calculated by differentiating the mass data versus time and they mean the rates at the maximum of DTG peak.

Furthermore, the reactivity test parameters such as heating, gas flow rate, and mass of the sample were determined based on the preliminary TG test results. Each measurement was also repeated to ensure the quality of measurement.

4. Conclusions

In coal-based chemical looping combustion technology, relatively inexpensive and both chemically and mechanically stable oxygen carrier materials are required. This is due to the fact that some of the oxygen carriers may be potentially removed together with the coal ash after combustion.

In this work, bimetallic supported with 20 wt.% addition of zirconia oxide Fe-Mn/Zr materials were synthesized. Cycling redox experiments enabled to evaluate the capacity over several cycles, and to confirm if the oxidized/reduced OCs can be recovered after

multiply redox reactions. The four Fe-Mn/Zr OCs with moderate manganese content (15–30 wt.%) may have a high potential as a CLOU material in CLC when the capacity is properly transferred to the fuel reactor.

Multiply methods used such as TGA, QMS, XRD, SEM, and EDS proved that the OC materials are CLC and CLOU capable together with supporting the mechanical properties to be extremely stable and durable mixed Fe–Mn oxides supported on ZrO₂ for potential practical utilization in CLOU and CLC processes. It was demonstrated as CLOU oxygen capacities were evolved from OC material structure with a moderate rate and required amount (up to 1.5 wt.%) to combust the hard coal.

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