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Combined oxides as oxygen carrier material for chemical-looping with oxygen uncoupling

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Abstract – Oxygen-carrier materials for chemical-looping with oxygen uncoupling (CLOU) must be capable to take up and release gas-phase O_2 at conditions relevant for generation of heat and power. In principle, the capability of a certain material to do so is determined by its thermodynamic properties. This paper provides an overview of the possibility to design feasible oxygen carrier materials from combined oxides, i.e. oxides with crystal structures that include several different cations. Relevant literature is reviewed and the thermodynamic properties and key characteristics of a few selected combined oxide systems are calculated and compared to experimental data. The general challenges and opportunities of the combined oxide concept are discussed. The focus is on materials with manganese as one of its components and the following families of compounds and solid solutions have been considered: $(Mn_yFe_{1-y})O_x$, $(Mn_ySi_{1-y})O_x$, $CaMnO_{3-\delta}$,$(Ni_yMn_{1-y})O_x$, $(Mn_yCu_{1-y})O_x$ and $(Mn_yMg_{1-y})O_x$.

1 Chemical-looping with oxygen uncoupling

Chemical-looping combustion (CLC) is an innovative method to oxidize fuels with inherent CO_2 sequestration. Two separate reactors are used, one air reactor (AR) and one fuel reactor (FR). A solid oxygen carrier (MeO_x/MeO_{x-1}) performs the task of transporting oxygen between the reactors. Direct contact between fuel and air is avoided, see Figure 1.

The oxygen carrier circulates between the two reactors. In the fuel reactor, it is reduced by the fuel, which in turn is oxidized to CO_2 and H_2O according to reaction (1). In the air reactor, it is oxidized to its initial state with O_2 from the air according to reaction (2). Combining reaction (1) and reaction (2) yields reaction (3), which is complete combustion of the fuel with O_2.

C_nH_m + (2n+½m) MeO_x → nCO_2 + (½m)H_2O + (2n+½m) MeO_{x-1} (1)

MeO_{1-x} + ½O_2 → MeO_x (2)

C_nH_m + (n+¼m)O_2 → nCO_2 + (½m)H_2O (3)

Chemical-looping combustion has several attractive features. The gas from the fuel reactor consists essentially of CO_2 and H_2O so condensation of steam to liquid water is all that is needed to obtain almost pure CO_2 for sequestration. A feasible design is to use a circulating fluidized bed reactor with oxygen-carrier particles as bed material, which is straightforward and available technology. Commonly proposed oxygen carrier materials include transition metal oxides such as NiO, Fe_2O_3, CuO or Mn_3O_4. The progress within the area of has been reviewed recently by Adanez et al. [1] and Lyngfelt [2].

In reaction (1), it was assumed that the fuel is in gas phase and that it reacts with the oxygen carrier in a gas-solid-reaction. However, with some oxygen carrier materials gas-phase O_2 can be released directly in the fuel reactor according to reaction (4).

MeO_x ↔ MeO_{1-x} + ½O_2 (4)

O_2 will be released until equilibrium for reaction (4) is obtained. If there is a fuel present it will react directly with released O_2 according to reaction (3), which will facilitate further O_2 release until all available fuel is consumed. The reduced oxygen carrier can then be recirculated to the air reactor where it is reoxidized according to reaction (2).

This reaction scheme described above is referred to as chemical-looping with oxygen uncoupling (CLOU), see Mattisson et al. [3]. The sum of reactions is identical to the one for chemical-looping combustion, but the mechanism by which the fuel is oxidized is different. In ordinary chemical-looping combustion, the oxidation of fuel takes place mainly via gas-solids reactions. So if the fuel is a solid such as coal, it has to be gasified in order to be able to react with the solid oxygen carrier. By contrast, in chemical-looping with oxygen uncoupling, the oxidation of the fuel can proceed by direct combustion. Leion et al. [4] have shown that oxidation of coke can be orders of magnitude faster using this reaction scheme compared to a conventional chemical-looping combustion process which relies on char gasification.

1.1 Aim of this study

The aim of this study is to provide an overview of the possibility to design oxygen carrier materials from combined oxides, i.e. oxides with structures that include several different cations.

2 Oxygen carriers for chemical-looping with oxygen uncoupling

The central requirement for an oxygen-carrier material for chemical-looping with oxygen uncoupling is that it should be capable of taking up and releasing gas-phase O_2 at conditions relevant for char combustion. This capability is dictated by the equilibrium O_2 partial pressure (p_{O2}) for reaction (4), which is different for different materials and also a function of parameters such as temperature and pressure.

In a real-world facility for power generation with a conventional Clausius-Rankine cycle, the O_2 concentration in the outlet of the air reactor would preferably be low. High excess air reduces the efficiency of the plant and increases costs. In this work it is assumed that the highest acceptable O_2 concentration in the gas from the air reactor is 5%, i.e. an excess air ratio of 20%, which is comparable to what is used in circulating fluidized bed boilers. This means that the equilibrium O_2 partial pressure for reaction (4) should not be higher than 5% at the desired air reactor temperature, else reoxidation will be impossible. Hence calculating this temperature ($T_{eq,PO2=5\%}$) provides the maximum air reactor temperature for a certain oxygen carrier.

As for the fuel reactor, high temperature equals a higher partial pressure of O_2 according to reaction (4) and faster overall reaction kinetics. As will be explained below, oxygen carriers for chemical-looping with oxygen uncoupling typically gives slightly exothermic reactions with fuel in the fuel reactor. It seems reasonable to assume that heat will be extracted in the air reactor to control the temperature here, while the fuel reactor will be allowed operate at similar or slightly higher temperature.

Depending on solids circulation and solids inventory, the O_2 release could well be higher than what is consumed by the fuel. This would then lead to the presence of oxygen in the gas from the fuel reactor. Thus, it can be assumed that operation with oxygen carriers that release oxygen will need proper control systems to avoid either excess of oxygen or unconverted fuel gas.

Since the reactions in the fuel reactor typically are exothermic, high solids circulation should not be necessary to maintain the overall heat balance. Instead, the minimum solids circulation will be determined by the oxygen carrier capacity (R_0) which is defined in equation (5), in which m_{ox} is the weight of the fully oxidized sample and m_{red} is the weight of the fully reduced.

$$R_0 = (m_{ox} - m_{red}) / m_{ox} \qquad (5)$$

Below is an overview over some binary and ternary oxide systems which have been identified as promising for the proposed application. All data and phase diagrams have either been calculated with the software FactSage 6.1 using the FToxid database, or in some case been taken from identified sources. The results are summarized in section 3 below.

2.1 Monometallic oxygen carriers

Although not the focus of this study, it should be mentioned that there are monometallic systems which could be feasible for the discussed application. CuO is commonly proposed and has been shown to release O_2 rapidly via reaction (6) at temperatures in the range of 850-950°C, see for example Leion et al. [4], Gayán et al. [5], Eyring et al. [6] and Arjmand et al. [7]. Further, Mn_2O_3 could release O_2 via reaction (7), but reoxidation is restricted to low temperatures where the rate of reaction appears to be too slow to be practically applicable [3]. Finally, Co_3O_4 could release O_2 via reaction (8), but this system looks unattractive due to unfavourable cost, health and environmental characteristics [3]. The equilibrium O_2 partial pressure for reactions (6-8) can be found in Figure 2.

$$4CuO \leftrightarrow 2Cu_2O + O_2 \qquad (6)$$

$$6Mn_2O_3 \leftrightarrow 4Mn_3O_4 + O_2 \qquad (7)$$

$$2Co_3O_4 \leftrightarrow 6CoO + O_2 \qquad (8)$$

2.2 $(Mn_yFe_{1-y})O_x$ combined oxides

The ternary system Mn-Fe-O has properties which make it exceptionally interesting for oxygen carrier applications. In fact, such oxides have already been proven to be capable of releasing considerable amounts of gas phase O_2, see Azimi et al. [8, 9, 10], Rydén et al. [11] and Shulman et al. [12]. This family of materials is believed to be resistant towards fuel impurities such as sulfur and could also be manufactured from cheap and relatively harmless raw materials.

A binary phase diagram of the $(Mn_yFe_{1-y})O_x$ system is shown in Figure 3. It can be seen that hematite (Fe_2O_3) and bixbyite $(Mn_yFe_{1-y})_2O_3$ are favored at lower temperature, while spinel phases $(Mn_yFe_{1-y})_3O_4$ are favored at higher temperature. At intermediate temperatures there is a two-phase area in which both forms coexist. The reaction of interest to chemical-looping with oxygen uncoupling is transition between bixbyite and spinel via reaction (9).

$$6(Mn,Fe)_2O_3 \leftrightarrow 4(Mn,Fe)_3O_4 + O_2 \qquad (9)$$

In Figure 3, it can be seen that if the surroundings has an O_2 partial pressure of 0.05 atm, reaction (9) goes to the right at temperatures over ≈1330°C for pure Fe_2O_3. The corresponding temperature for pure Mn_2O_3 is ≈800°C. For mixtures of the two, O_2 release happen at intermediate temperatures. The height of the two-phase area in Figure 3 corresponds to the change in temperature that will be required to force reaction (9) into completion. The reaction may also be accomplished by a change in O_2 partial pressure, and the needed change should correspond to the required change in temperature. This suggests that mixtures with Mn/(Mn+Fe) of 0.5-0.8 would be particularly attractive for chemical-looping with oxygen uncoupling, since small changes in the surroundings would result in considerable O_2 release.

Figure 4 shows equilibrium O_2 partial pressure as function of temperature over $(Mn_{0.8}Fe_{0.2})O_x$ and $(Mn_{0.5}Fe_{0.5})O_x$. It can be seen that the combined spinel $(Mn_{0.8}Fe_{0.2})_3O_4$ can be completely oxidized to bixbyite $(Mn_{0.8}Fe_{0.2})_2O_3$ by 5% O_2 at temperatures below ≈890°C, while the corresponding temperature for $(Mn_{0.5}Fe_{0.5})O_x$ is ≈940°C. Increasing the iron content above 50% would increase the possible temperature of operation further but also widen the two-phase area, which likely is undesirable.

$(Mn_yFe_{1-y})O_x$ combined oxides has been examined as oxygen carrier for chemical-looping applications by Azimi et al. [8, 9, 10], Rydén et al. [11], Shulman et al. [12], Lambert et al. [13], and Ksepko et al. [14]. Studies [8-12] are all in good agreement with the reasoning presented above. In particular the study by Azimi et al. [8] which was conducted according to the principles proposed in this paper using $(Mn_{0.8}Fe_{0.2})O_x$ as oxygen carrier, showed very fast O_2 uncoupling and rapid oxidation of both methane and wood char already at 850°C.

2.3 $(Mn_ySi_{1-y})O_x$ combined oxides

Manganese and silica oxides are cheap, could be expected to be inert towards sulfur at relevant temperatures and have low health and environmental impact. A binary phase diagram of this system is shown in Figure 5. It can be seen that the expected reaction mechanism for O_2 release and uptake is different depending on the material composition.

With Si/(Mn+Si) below 0.14 the system behaves similar to the pure manganese oxide system. If the surroundings have an p_{O2} of 0.05 atm, bixbyite Mn_2O_3 *(M)*, is reduced to hausmannite spinel Mn_3O_4 *(S)* via reaction (7) at temperatures above ≈800°C. Temperature for the transition increases as function of the Si content, which is expected to be present mainly as braunite Mn_7SiO_{12} *(B)*. The lower left corner of Figure 5 differs slightly from the classic studies by Muan et al. [15, 16], so the precise temperature for how much Si that is needed to increase the decomposition temperature in this region is somewhat unclear.

With Si/(Mn+Si) above 0.14 the mechanism for O_2 release is decomposition of braunite to *R* rhodonite $MnSiO_3$ *(R)*, reaction (10). With p_{O2}=0.05 atm, reaction (10) goes to the right above ≈980°C. Excess Si would in this case be inert and present as tridymite SiO_2 *(T)*.

$$({}^{2}/_{3})Mn_7SiO_{12} + 4SiO_2 \leftrightarrow ({}^{14}/_{3})MnSiO_3 + O_2 \qquad (10)$$

According to Figure 5, Reaction (10) can only go into completion in the first step if Si/(Mn+Si) is equal to 0.50, otherwise braunite or tridymite will be in excess. For Si/(Mn+Si) of 0.14-0.50, further O_2 release instead take place from conversion of rhodonite to tephroite Mn_2SiO_4 *(E)*, reaction (11), which takes place in a second step at higher temperatures.

$$({}^{10}/_{3})MnSiO_3 + ({}^{2}/_{3})Mn_7SiO_{12} \leftrightarrow 4Mn_2SiO_4 + O_2 \qquad (11)$$

Figure 6 show equilibrium partial pressure of O_2 as function of temperature over $(Mn_ySi_{1-y})O_x$ combined oxides with Si/(Mn+Si) larger than 0.14. Complete oxidation with 5% O_2 should be possible at temperatures below ≈980°C, which consequently should constitute a suitable air reactor temperature. Figure 6 is in good agreement with data provided by Muan et al. [16].

Up to this point, $(Mn_ySi_{1-y})O_x$ combined oxides has not been widely examined as oxygen carrier for chemical-looping applications. Calvo [17] and Jing et al. [18] examined O_2 release and reactivity with fuel gases at temperatures up to 1100°C for such oxygen carriers with SiO_2 content ranging from 2-50 wt%. All samples were found to release small amounts of O_2, albeit some only at very high temperatures. In both studies reproducibility appears to have been a problem. At some occasions considerable O_2 release was reported for initial experiments, but the effect diminished after several cycles or after reduction with fuel [17]. Other materials which initially did not release O_2 in N_2 at 900°C were found to release minor amounts following reduction with fuel and reoxidation [18]. At very high temperatures, particles with 30 wt% SiO_2 were found to release O_2 more or less as suggested for reaction (11) in Figure 6, but full oxidation to Mn_7SiO_{12} apparently was not possible [17]. The general impression for these two series of experiments is that oxidation to Mn_7SiO_{12}, Mn_2O_3 and SiO_2 may have been slow or limited. Johansson et al. [19] examined oxygen carrier particles with Si/(Mn+Si) of 0.68, which were calcined in air at 950-1300°C. No O_2 release in inert atmosphere was reported, but the phase composition of the particles was consistent with Figure 5, i.e. particles calcined at 950-1100°C consisted of Mn_7SiO_{12} and SiO_2, while particles calcined at 1200-1300°C also contained $MnSiO_3$. Shulman et al. [12] prepared oxygen carriers with Si/(Mn+Si) of 0.24 which were calcined in air at 950-1100°C. The resulting particles reportedly consisted of Mn_2O_3 and SiO_2 and released O_2 during fluidization with N_2, following oxidation with 10% O_2 in N_2 The O_2 release was quite high at 850°C, up to 2.5%, only to fall back to almost zero at 900°C. Lack of O_2 release at 900°C suggests that the mechanism could have been reaction (7), for which reoxidation to Mn_2O_3 should not have been possible at 900°C using the described process conditions. In any case, these observations as well as the phase composition of the fresh particles is inconsistent with Figures 5-6.

To summarize; thermodynamic analysis suggests that $(Mn_ySi_{1-y})O_x$ combined oxides could work excellently as oxygen carrier for chemical-looping with oxygen uncoupling. There is limited experimental experience with this kind of materials though and the results fit poorly with theoretical analysis.

2.4 $CaMnO_{3-\delta}$ and other materials of perovskite structure

Materials of perovskite structure have a unit cell which can be written $ABO_{3-\delta}$, in which A is a large cation and B is a smaller cation. The δ-factor expresses the degree of oxygen deficiency in the structure, and is zero for a perfect structure.

There are countless possibilities to synthesize materials of perovskite structure. The A and B sites does not have to consist of one single type of ions. Doping of the A and B site with one or more type of ions is possible as long as the dopants have similar ionic radii and oxidation state as the main atom. Generally speaking, the B site can be selected among most transition metal ions. Good candidates for the application chemical-looping combustion could be for example manganese, iron and titania, albeit small amounts of more expensive materials such as copper, nickel or cobalt could be included in the structure as well. The A site needs to have much larger ionic radii and there are less options. Calcium appears to be the most attractive due to good availability and low cost, with the most commonly examined alternatives being lanthanum and strontium. Finally, the sum of the expected oxidation number of the A and B site should be in the range 5-6, which would yield materials with a δ-factor of 0.5-0. The formability of perovskites has been extensively reviewed by Li et al. [20].

Materials of perovskite structure are interesting for chemical-looping applications because δ can be increased or reduced by altering factors in the surroundings such as temperature, pressure or O_2 fugacity. The surroundings in a chemical-looping air reactor are oxidative, while they are reductive in the fuel reactor. Therefore δ_{ar} will be smaller and δ_{fr} will be larger. The amount of O_2 available for oxidation of fuel can be written as $(\delta_{fr} - \delta_{ar})$, see reaction (12).

$$ABO_{3-\delta ar} \leftrightarrow ABO_{3-\delta fr} + \tfrac{1}{2}(\delta_{fr}-\delta_{ar})\ O_2 \qquad (12)$$

Not all materials with perovskite structure undergo reaction (12) at conditions suitable for chemical-looping combustion. Instead, the properties of a certain material will depend on nature of the A and B sites. One proposed material composition which has proven to be of interests for chemical looping combustion is calcium manganite $CaMnO_{3-\delta}$, and slightly altered variants thereof. Rydén et al. [21] examined $CaMn_{0.875}Ti_{0.125}O_{3-\delta}$ in a small circulating fluidized bed reactor and reported good fluidization behavior, stable operation, O_2 release in inert atmosphere and that complete conversion of CH_4 was achievable. Leion et al. [22] examined $CaMn_{1-x}Ti_{xO3-\delta}$ both in a thermo gravimetric analyzer and in batch fluidized bed reactor. The materials were found to have high reactivity with CH_4 and petroleum coke and released O_2 in gas phase when fluidized with N_2. Further, it was possible to remove as much as 8-9 wt% O_2 from the particles without collapsing the perovskite structure which suggests a feasible operating span ranging from δ of 0 to about 0.7. Hallberg et al. [23] examined $CaMnO_{3-\delta}$ oxygen carriers with the B site doped with Fe, Ti, and Mg with good results, while Fossdal et al. [24] successfully manufactured $CaMnO_{3-\delta}$ oxygen carrier materials from manganese ore and calcium hydroxide.

With respect to direct release of gas phase O_2 in inert atmosphere, different dynamics could be expected compared to materials which undergo distinct phase changes. Figure 7 describes δ at equilibrium as function of O_2 partial pressure. It can be seen that O_2 could be expected to be released at comparably high concentrations initially, when δ is at its minimum. But as O_2 is removed from the perovskite structure and δ increases, the obtained O_2 partial pressure is continuously reduced in a logarithmic fashion. This behavior has been documented for example by Leion et al. [22] and Hallberg et al. [23] during experiments in batch fluidized bed reactor.

It is evident from Figure 7 that the higher O_2 partial pressure which is used for oxidation, the more O_2 can be transported to an inert or low O_2 atmosphere. For example, oxidation with 21% O_2 and $\log(pO_2/atm)=-0.678$ at 950°C and atmospheric pressure would result in $CaMnO_{2.95}$, while oxidation with 5% O_2 and $\log(p_{O2}/atm)=-1.301$ at the same conditions would result in $CaMnO_{2.92}$. Consider a second process step in which gaseous O_2 would be released in an atmosphere with 0.1% O_2 and $\log(p_{O2}/atm)=-3.000$ and the final product could be expected to be $CaMnO_{2.85}$. In the first case, the O_2 release according to reaction (12) would be $½\cdot(0.15-0.05)=0.050$ mol O_2 (≈1.1 wt%), compared to $½\cdot(0.15-0.08)=0.035$ mol O_2 (≈0.8 wt%). This mechanism described has been verified by Rydén et al. [21] by conducting experiments in a small circulating fluidized bed reactor, in which it was seen that O_2 release was considerably higher when oxidizing $CaMn_{0.875}Ti_{0.125}O_{3-\delta}$ with air rather than with a mixture consisting of 5% O_2 and 95% N_2.

2.5 $(Mn_yNi_{1-y})O_x$ combined oxides

Shulman et al. [12] examined oxygen carrier particles consisting of 80 wt% Mn_3O_4 and 20 wt% NiO calcined in air at 950-1300°C, all of which reportedly consisted of mostly of $NiMn_2O_4$ spinel, as per XRD of fresh materials. During fluidization with N_2 small amounts of O_2 were released at 810-900°C. The likely mechanism is decomposition into manganese-rich spinel $(Mn_yNi_{1-y})_3O_4$ and nickel-rich $(Ni_yMn_{1-y})O$ of rock-salt structure, reaction (13), as have been reported by Csete de Györgyfalva and Reaney [26].

$$6NiMn_2O_4 \leftrightarrow 6NiO + 4Mn_3O_4 + O_2 \quad (13)$$

The reported temperature of decomposition of $NiMn_2O_4$ in air according to reaction (13) is 907°C [26]. This suggests that reoxidation could be a problem when using low O_2 concentrations. Shulman et al. [12] were capable to oxidize to oxidize particles using 10% O_2 in N_2 at 900°C though. In general, these results appear to be in good agreement with the phase diagram provided by Golikov and Balakirev [27].

Despite these promising results, the allure of $(Mn_yNi_{1-y})O_x$ combined oxides as oxygen carrier for chemical-looping applications is not necessarily high. Ni is expensive and carcinogenic and would probably be more useful as monometallic oxygen carrier since direct reduction of NiO yields metallic Ni, which is well-known to possess some interesting catalytic properties.

2.6 $(Mn_yCu_{1-y})O_x$ combined oxides

Since both manganese and copper oxides individually has properties which makes them interesting for chemical-looping with oxygen uncoupling, it could be expected that $(Mn_yCu_{1-y})O_x$ combined oxides should form compounds or solid solutions capable of releasing O_2 in the relevant temperature span as well. Azad et al. [28] synthesized particles with a Mn/Cu ratio of 2 via extrusion and calcination at 950°C. XRD analysis showed that the fresh and oxidized material consisted of one or several combined spinel phases $(Mn_yCu_{1-y})_3O_4$, while particles reduced with fuel gas at 850°C consisted mostly of cerdnerite $CuMnO_2$ and hausmannite Mn_3O_4. The particles provided high reactivity with CH_4 and released up to 2.5% O_2 when fluidized with N_2 at 850°C. Reaction (14) illustrates the expected reaction mechanism for the stoichiometric spinel:

$$3CuMn_2O_4 \leftrightarrow 3CuMnO_2 + Mn_3O_4 + O_2 \quad (14)$$

These observations are in accordance with the phase diagram suggested by Driessens and Rieck [29], whose work also indicates that all $(Mn_yCu_{1-y})O_x$ combined oxides could release gas phase O_2 at relevant temperatures, albeit via complex reactions schemes and at lower temperatures than for pure CuO. Whether this option could be interesting for chemical-looping applications remains to be explored.

2.7 $(Mn_yMg_{1-y})O_x$ combined oxides

The following solid solutions and compounds are said to exist below 1000°C in the Mn-Mg-O ternary system according to Valverde-Diez and Grande-Fernándes [30]:

a) Compounds Mg_6MnO_8, Mg_2MnO_4 and $MgMn_2O_4$.

b) Solid solution $(Mg_xMn_{3-x})O_4$ with $0<x<2$ which has a spinel structure.

c) Solid solution $(Mg_xMn_{1-x})O$ with $0<x<0.33$ which has a rock-salt structure.

Shulman et al. [31] successfully prepared several oxygen carrier particles with Mg/Mn ratio of 2 and calcination in air at 1100-1300°C, all of which reportedly consisted of Mg_2MnO_4, as per XRD analysis of fresh particles. This corresponds to $2MgO \cdot MnO_2$ and an oxidation state of manganese ions of Mn^{+4}, which seems quite remarkable. In inert atmosphere and elevated temperature, O_2 could be expected to be released via reaction (15), which illustrates reduced solubility of Mg in the spinel solid solution. The simplified reactions (16-17) is for stoichiometric compounds:

$$Mg_2MnO_4 \leftrightarrow [1-(1/(1+x))]\,(Mg_{2-x}Mn_{1+x})O_4 + [1+x]\,MgO + [1/(1+x)]\,O_2 \qquad (15)$$

$$4Mg_2MnO_4 \leftrightarrow 2MgMn_2O_4 + 6MgO + O_2 \qquad (16)$$

$$6MgMn_2O_4 \leftrightarrow 4Mn_3O_4 + 6MgO + O_2 \qquad (17)$$

From the work of Shulman et al. [31] and earlier work with this system by Oliveira and Brett [32], it seems likely that reaction (15) takes place at higher temperatures than for monometallic manganese oxides and via a sliding equilibrium for O_2 partial pressure depending on the factor x in reaction (15). Further work will be needed in order to provide a better understanding of this oxide system though.

3 Results and discussion

The focus of this article has been on combined oxides with manganese as one of its constituents. That is not to say that other ternary systems do not exhibit this kind of properties. We believe that the case for manganese is pretty good though, since it is a cheap and comparably benign transition metal which forms compounds with a large number of other elements and which ions can exist in a remarkably high number of oxidation states, from Mn^{2+} to Mn^{7+}. A summary of the most basic properties for the materials suggested in this work can be found in Table 1 on the following page.

In Table 1, it can be seen that most manganese based combined oxides has considerably lower oxygen carrying capacity R_0, compared to CuO. Values of 2-3 wt% should still be sufficient for practical applications though.

ΔH for O_2 release typically is in the range 250-325 kJ/mol O_2, i.e. pretty similar to that of CuO. If compared to the enthalpy of combustion at 900°C for methane (-401 kJ/mol O_2) and carbon (-379 kJ/mol O_2), it is evident that the overall reaction in the fuel reactor typically will be slightly exothermic. As explained above, this could be favorable since it simplifies closure of the heat balance for the fuel reactor. It shall be pointed out that endothermic reaction in the fuel reactor using oxygen carriers with O_2 release is a possibility, and should be the case for example if Co_3O_4–CoO is used, as can be seen in Table 1.

Of the suggested systems, some could be suspicable to deactivation by fuel impurities. The sulfur tolerance of oxygen carriers containing for example Ca, Mg and Ni is unknown but questionable, since formation of stable sulfates and sulfides would be favored at relevant temperatures. The effect of sulfur on such oxygen carriers will need to be carefully considered and experimentally examined.

Factors which have not been considered in this paper are for example mechanical and chemical stability of multiphase materials, which could be problematic. Compatibility of the active phase with inert support materials would also get more complicated the more elements are included in the oxygen carrier. Manufacturing would probably not be more complicated for combined oxides compared to monometallic, although better homogenization and higher calcination temperatures may be necessary to obtain the desired materials.

4 Conclusions

This paper has provided an overview of the possibility to design feasible oxygen carrier materials from combined oxides. Current literature has been reviewed and complemented with thermodynamic calculations. It can be concluded that there are several opportunities with the most interesting ones being materials based on the general formulas $(Mn_yFe_{1-y})O_x$, $(Mn_ySi_{1-y})O_x$ and $CaMnO_{3-\delta}$.

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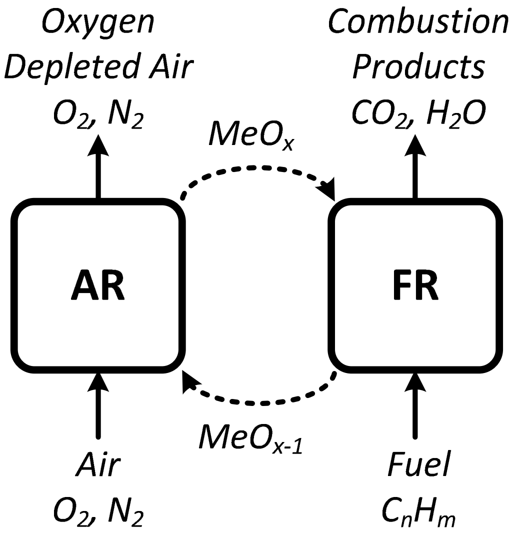

Figure 1: Schematic description of chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU).

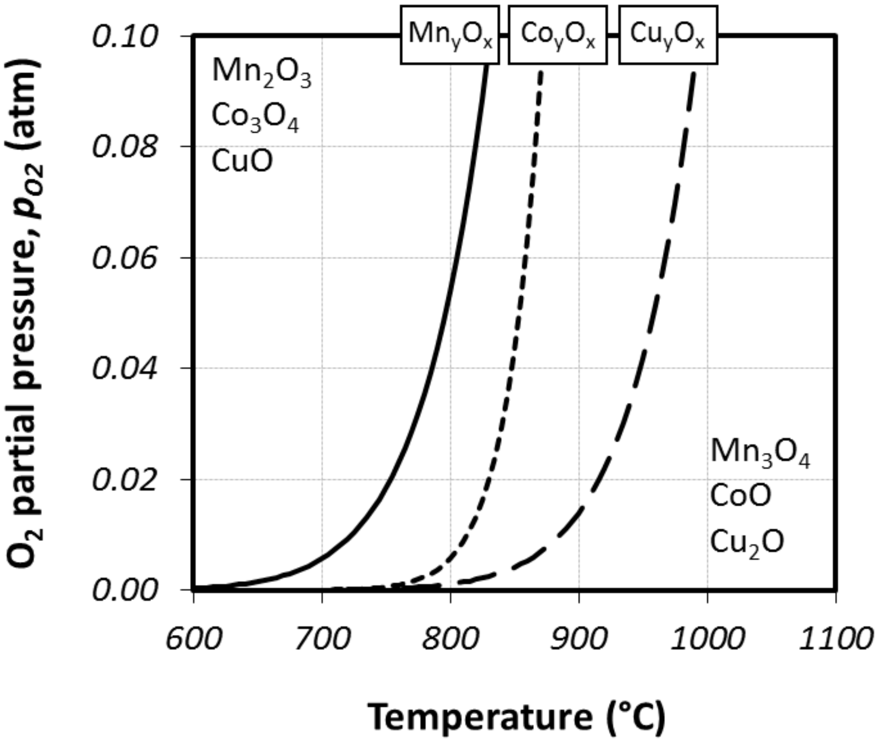

Figure 2: Equilibrium O_2 partial pressure of as function of temperature for selected monometallic oxygen carriers.

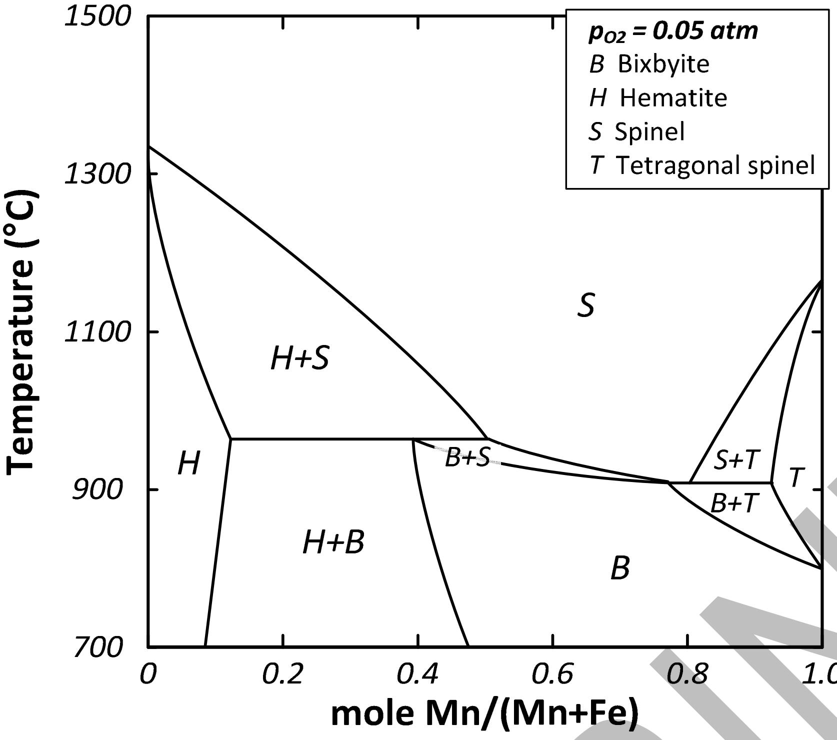

Figure 3: Binary phase diagram of $(Mn_yFe_{1-y})O_x$ in an atmosphere with an O_2 partial pressure of 0.05 atm.

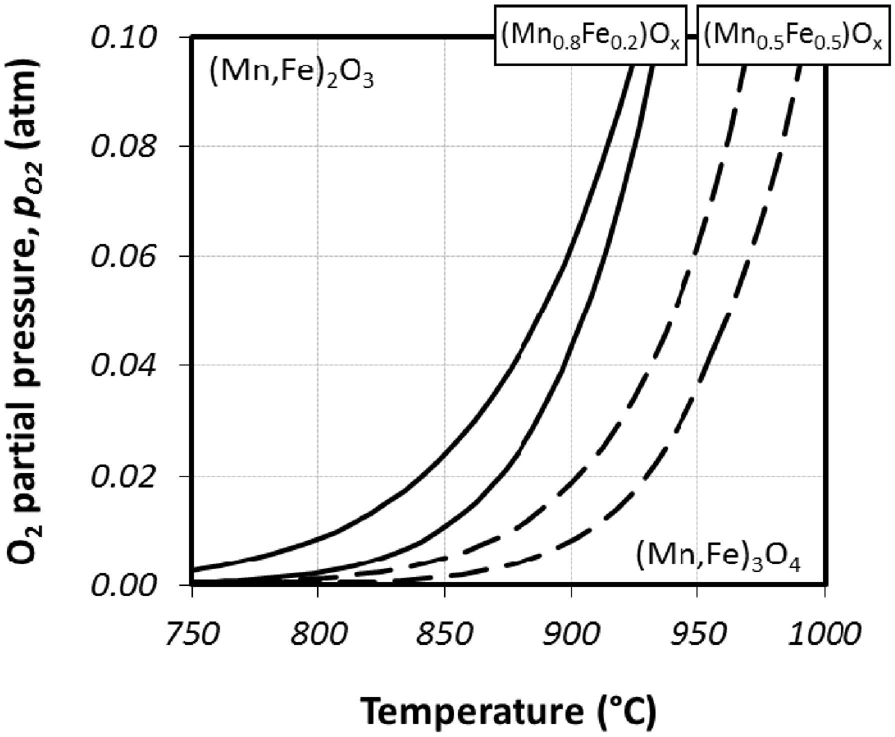

Figure 4: p_{O2} as function of temperature over (Mn$_x$Fe$_{1-x}$)O$_x$. Area enclosed by each set of curves represents the two-phase area where bixbyite and spinel phases coexists.

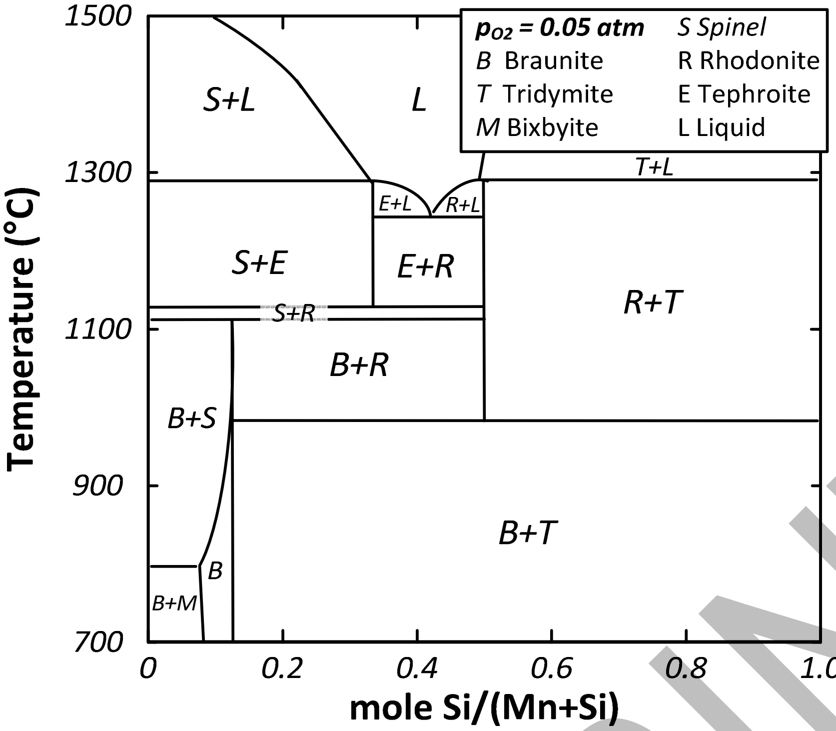

Figure 5: Binary phase diagram of $(Mn_ySi_{1-y})O_x$ in an atmosphere with an O_2 partial pressure of 0.05 atm.

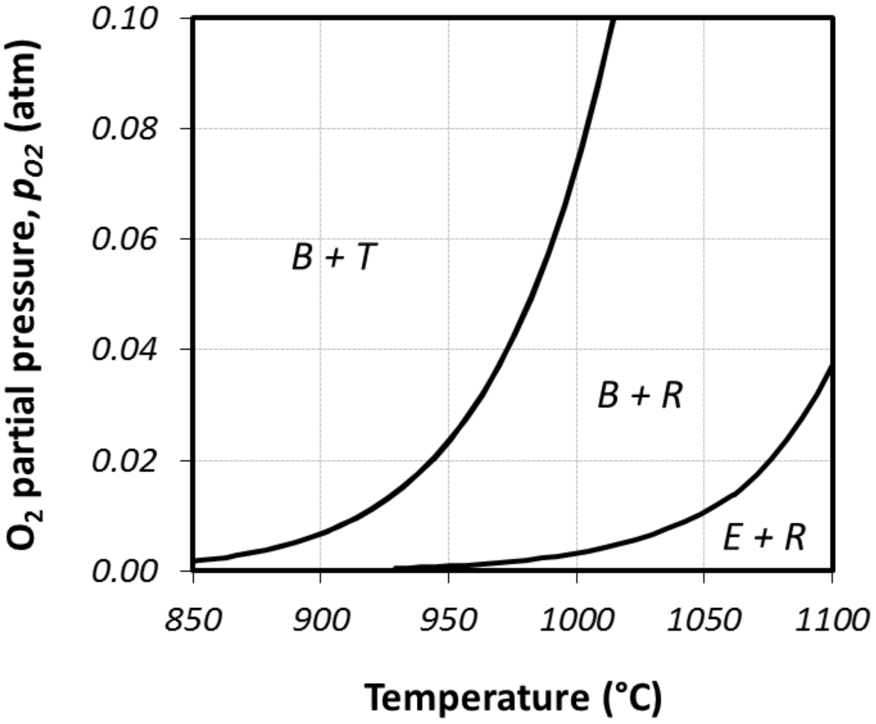

Figure 6: p_{O2} as function of temperature over $(Mn_ySi_{1-y})O_x$ combined oxides with Si/(Mn+Si) above 0.14. Transition to Mn_2SiO_4 only valid for Si/(Mn+Si) 0.14-0.50.

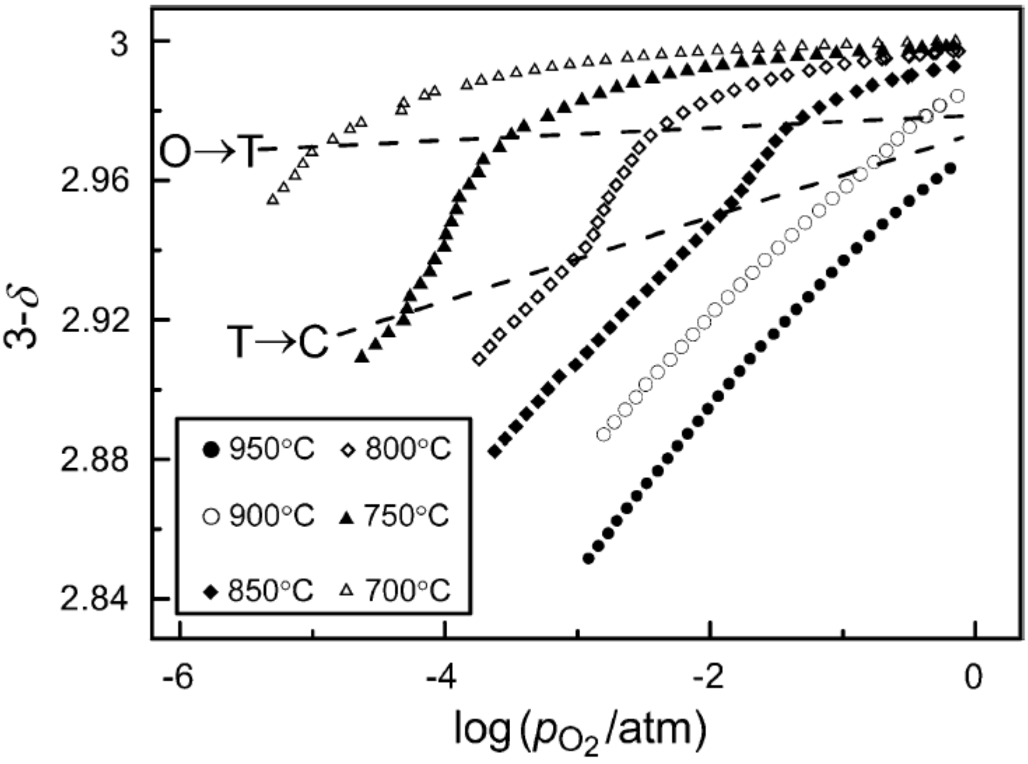

Figure 7: Equilibrium δ as function of O_2 partial pressure for $CaMnO_{3-\delta}$ at 700-950℃ measured by coulometric titration by Leonidova et. al [25].

Table 1: Summary of key characteristics for proposed oxygen carrier materials.

Reaction	**R_0 (wt%)**	**ΔH (kJ/mol O_2)**	**$T_{eq,pO2=5\%}$ (°C)**	**$T_{eq,pO2=21\%}$ (°C)**
$4CuO \leftrightarrow 2Cu_2O + O_2$	10.06	261	959	1032
$6Mn_2O_3 \leftrightarrow 4Mn_3O4 + O_2$	3.38	195	796	871
$2Co_3O_4 \leftrightarrow 6CoO + O_2$	6.64	408	854	893
$6(Mn_{0.8}Fe_{0.2})_2O_3 \leftrightarrow 4(Mn_{0.8}Fe_{0.2})_3O_4 + O_2$	3.37	254	≈890	≈965
$6(Mn_{0.5}Fe_{0.5})_2O_3 \leftrightarrow 4(Mn_{0.5}Fe_{0.5})_3O_4 + O_2$	3.36	344	≈940	≈1005
$(2/3)Mn_7SiO_{12} + 4SiO_2 \leftrightarrow (14/3)MnSiO_3 + O_2$	4.15	315 [33]	≈983	≈1050
$(10/3)MnSiO_3 + (2/3)Mn_7SiO_{12} \leftrightarrow 4Mn_2SiO_4 + O_2$	3.81	319 [33]	>1100	>1100
$25CaMnO_{2.92} \leftrightarrow 25CaMnO_{2.84} + O_2$	0.90	325 [34]	na	na
$5CaMnO_{2.92} \leftrightarrow 5CaMnO_{2.52} + O_2$	4.52	325 [34]	na	na
$6NiMn_2O_4 \leftrightarrow 6NiO + 4Mn_3O_4 + O_2$	2.29	Unavailable	<<907	≈907 [26]
$3CuMn_2O_4 \leftrightarrow 3CuMnO_2 + Mn_3O_4 + O_2$	4.49	Unavailable	<<990	≈990 [29]
$4Mg_2MnO_4 \leftrightarrow 2MgMn_2O_4 + 6MgO + O_2$	4.77	Unavailable	na	na
$6MgMn_2O_4 \leftrightarrow 4Mn_3O_4 + 6MgO + O_2$	2.69	Unavailable	na	na