

Prospects of Al₂O₃ and MgAl₂O₄-Supported CuO Oxygen Carriers in Chemical-Looping Combustion (CLC) and Chemical-Looping with Oxygen Uncoupling (CLOU)

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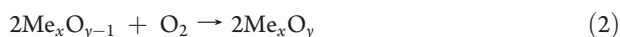
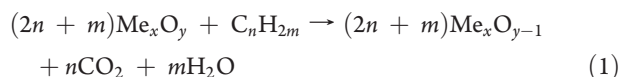
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ABSTRACT: The chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) processes are attractive solutions for efficient combustion with direct separation of carbon dioxide. In this work, the feasibility of CuO supported on Al₂O₃ and MgAl₂O₄ for CLC and CLOU processes is investigated. The oxygen carriers were produced by freeze-granulation and calcined at 950 and 1050 °C. The chemical-looping characteristics were evaluated in a laboratory-scale fluidized bed at 900 and 925 °C under alternating reducing and oxidizing conditions. Tendencies toward agglomeration, defluidization, and loss of active phase were analyzed by changing the experimental process variables, such as reaction time, temperature, and reducing and inert environments. Complete conversion of methane was obtained for all oxygen carriers investigated in this work. Three out of four oxygen carriers also featured the rapid release of oxygen in an inert environment (CLOU). In the case of Al₂O₃ as support, a CLC and a CLOU oxygen carrier were obtained depending on the calcination temperature. In addition, analyses of the CuO-Al₂O₃ phase equilibria system under oxidizing and reducing conditions have been carried out. At the investigated temperatures, it is inferred for the case of Al₂O₃ as support that part of the active phase (either CuO or CuAl₂O₄) is bound as CuAlO₂ during incomplete reduction with slow kinetics for reoxidation. However, when complete reduction is attained, the original active phase composition is rejuvenated upon oxidation. As a result, the use of CuAl₂O₄ is suggested for CLC processes from the point of agglomeration and attrition-free functioning of the oxygen carrier. In the case of MgAl₂O₄ as support, the oxygen carrier exhibited a stable oxygen-releasing behavior due to the existence of relatively intact CuO. Together with the absence of agglomeration and major morphological changes, the use of MgAl₂O₄-supported CuO is suggested as a suitable oxygen carrier for CLOU processes.

1. INTRODUCTION

As suggested by the intergovernmental panel on climate control (IPCC), a 50–85% reduction in total CO₂ emission by 2050 is mandated to limit the anticipated global temperature rise to below 2 °C.¹ A number of alternative technologies have been proposed to mitigate the rising levels of carbon dioxide in the atmosphere. Among these, carbon capture and storage (CCS) is considered promising.

The chemical-looping combustion (CLC) process allows intrinsic separation of pure CO₂ from a hydrocarbon fuel combustion process. In a CLC system as proposed by Lyngfelt et al.,² two reactors, viz., fuel and air are interconnected. When fuel and air are introduced into the respective reactor, the following reactions occur:



Here Me_xO_y and Me_xO_{y-1} are the fully oxidized and reduced forms of the oxygen carrier. The scheme of the process is shown in Figure 1. In case of complete conversion, the exhaust stream from the fuel reactor consists of only CO₂ and H₂O, from which

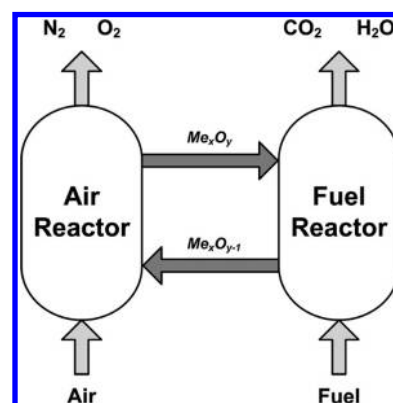


Figure 1. Scheme of the chemical-looping combustion (CLC) process.

pure CO₂ could be obtained after condensation of water. The reduced form of the oxygen carrier, Me_xO_{y-1}, is then transferred to the air reactor where it is reoxidized by air making it ready for the next cycle. The oxidation reaction is always exothermic while

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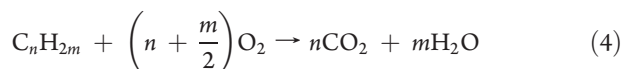
the reduction reaction can be exothermic or endothermic depending on the nature of the carrier and the fuel.³ However, the sum of the heat from reactions 1 and 2 is the same as for conventional combustion. Thus the CLC process does not entail additional cost or energy for CO₂ separation.

The reactivity of the oxygen carrier during oxidation and reduction cycles and the ability to fully convert the fuel are among the most sought-after criteria. In addition, their thermal stability, mechanical strength, fluidizability, and resistance to attrition and agglomeration are important. In order to achieve this, the active phase is often mixed with an inert support such as TiO₂, SiO₂, ZrO₂, Al₂O₃, or MgAl₂O₄.⁴

The CLC process could also be achieved through a modification known as chemical-looping with oxygen uncoupling (CLOU).⁵ In comparison to CLC where the reduction of oxygen carrier and oxidation of the gaseous fuel generally occurs in a single step, an additional step is needed in CLOU for the release of gaseous oxygen from the carrier prior to conversion of the fuel according to



This is followed by the normal combustion of the fuel via



The reduced oxygen carrier is transferred to the air reactor for reoxidation. The net heat of reaction for CLOU processes is the same as CLC; only the mechanism by which oxygen is accessed by the fuel differs. However when using solid fuels like coal, the CLOU process avoids the slow gasification of the solid fuel needed to produce syngas as a prerequisite for the reaction with the oxygen carrier.⁶ The oxygen carrier in CLOU must be able to release and take up O₂ at temperatures suitable for the process, viz. 800 to 1200 °C. This in turn imposes additional thermodynamic and kinetic requirements on the selected oxygen carrier.

Oxides of transition metals (Mn, Fe, Co, Ni, and Cu), their mixtures, and a range of natural ores have been used as oxygen carriers in CLC.⁴ Copper-oxide has received a great deal of attention as an efficient oxygen carrier, owing to its high reactivity and oxygen transport capacity and absence of thermodynamic limitation for complete combustion of the fuel. Research has been conducted using copper-oxide as CLC oxygen carrier and methane as fuel in fluidized and fixed bed batch reactors,^{7–11} continuous operations,^{12–15} and thermogravimetric studies,^{16–21} with and without the supports mentioned above. Among various supports for CuO oxygen carriers, Al₂O₃ has received considerable attention.^{10–14,19,20,22}

In addition, CuO decomposes to Cu₂O when the concentration of surrounding oxygen is lower than the equilibrium concentration. As a result, oxygen is released thereby allowing CLOU to take effect. For temperatures of 900 and 925 °C, this occurs at oxygen concentrations below 1.5 and 2.7%, respectively.⁶ Thus, from a CLOU point of view, the optimum temperature of the air reactor is likely in the range of 900–925 °C. Some investigations have also attempted to utilize CuO as a CLOU oxygen carrier for the combustion of solid fuels.^{6,23–25}

Despite these attractive features, use of CuO as an oxygen carrier is not without limitations. For example, copper-oxide suffers from the tendency toward agglomeration¹⁰ upon full

reduction due to rather low melting temperature of elemental copper (1085 °C). Thus the use of low-CuO content (less than 20 wt%) oxygen carriers was suggested to avoid agglomeration.¹⁰ For the same reason, most of the studies are limited to lower operating temperatures (800–850 °C), however with a few exceptions.^{12,13} Although full conversion of methane is achieved even at 800 °C, a higher temperature in the fuel reactor is favorable as it increases the equilibrium partial pressure of CuO/Cu₂O, which accompanies the rapid release of oxygen and therefore a higher reactivity.

Moreover in case of Al₂O₃ as support, CuO interacts with Al₂O₃ either during sample synthesis or in the reactors during operation resulting in partial loss of the active phase.^{7,10,12–14,18} Efforts have been made to hinder this interaction by addition of impurities to the CuO–Al₂O₃ mixture, so that free CuO is retained in the bulk.¹²

In cognizance of the potential of copper-based systems as CLC and CLOU materials, a study was undertaken to address two issues concerning the role of Al₂O₃ and MgAl₂O₄ as a support for CuO in CLC and CLOU applications. Initially, to ascertain a suitable phase boundary in the pseudobinary CuO–Al₂O₃ system for it to behave as a CLC material in light of the fact that there are strong interactions between the two at the typical processing temperatures. Second, to investigate the suitability of MgAl₂O₄ instead as a support where such active material-support interaction is absent or limited and thus, CuO can function as a suitable CLOU material.

2. EXPERIMENTAL SECTION

2.1. Preparation of Oxygen Carriers. The oxygen carriers used in this investigation and their physical properties are summarized in Table 1. The particles were manufactured by freeze-granulation. Here, a water-based slurry of CuO and support powders (α -Al₂O₃ and MgAl₂O₄) with weight ratio of 40/60 along with small amount of dispersant (Dolapix PC21) is prepared. The mixture is then ball milled for 24 h and binder (Polyvinyl Alcohol) is added prior to granulation. The slurry is pumped through a spray nozzle and into liquid nitrogen to form spherical particles upon instantaneous freezing. The samples were calcined at 950 and 1050 °C for 6 h at a ramp rate of 5 °C/min and then sieved through stainless steel screens to yield particles in the range of 125–180 μm . The calcination temperature is given in the abbreviation for each sample as shown in Table 1.

2.2. Characterization of Oxygen Carriers. The oxygen carriers were analyzed before and after the experiments using powder X-ray diffraction (Siemens, DS5000 Diffractometer) with Cu K α radiations. The morphological investigation was carried out with an environmental scanning electron microscope (ESEM) fitted with a field emission gun (FEI, Quanta 200). The BET surface area of the particles was evaluated by N₂-absorption (Micromeritics, TriStar 3000). The apparent density of the samples, sized 125–180 μm , was measured assuming a void factor of 0.37 as the theoretical voidage of a packed bed with uniform spherical particles. The crushing strength of the particles was also measured as the strength needed to fracture the particles ranging within 180–250 μm for an average of 30 tests per sample using a digital force gauge (Shimpo, FGN-5). The crushing strength was found to be less than 0.5 N for all the samples. In some cases particles with a crushing strength below 1 N are considered too soft.²⁶ However, this did not cause any problem such as defluidization in the reactor as determined by the pressure drop in the bed. Nonetheless for use in a full scale plant, the crushing strength may need to be increased which could be done by either increasing the sintering time or temperature.

Table 1. Oxygen Carrier Properties

oxygen carrier	C4A-950	C4A-1050	C4MA-950	C4MA-1050
theoretical CuO content [wt%]		40		
support phase	α -Al ₂ O ₃ (A16SG, Alcoa)	MgAl ₂ O ₄ (S30CR, Baikowski)		
size interval of particles [μ m]		125–180		
apparent density [g/cm ³]	2.4	1.8	2.1	2.6
BET specific surface area [m ² /g]	4.1	4.2	11.7	6.5
crushing strength [N]		<0.5		

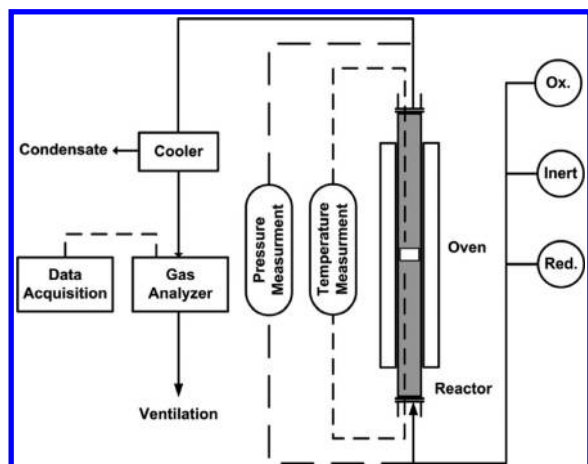


Figure 2. Scheme of the experimental setup used in this investigation.

2.3. Experimental Procedure. Experiments were carried out in a quartz fluidized-bed reactor, 870 mm long and 22 mm in inner diameter. A porous quartz plate was placed at a height of 370 mm from the bottom and the reactor temperature was measured with chromel–alumel (type K) thermocouples sheathed in inconel-600 clad located about 5 mm below and 25 mm above the plate. Honeywell pressure transducers with a frequency of 20 Hz were used to measure pressure differences over the bed. The scheme of the experimental setup used in this investigation is shown in Figure 2.

Fifteen g of the oxygen carrier were placed on the porous plate and then exposed to alternating oxidizing and reducing conditions. The experiment was initiated by heating the reactor to 900 °C in 5% O₂ in N₂ to ensure full oxidation of the carrier prior to the experiments. The use of 5% O₂ is to be close to the expected oxygen deficient condition at the air reactor's outlet and also to obviate large temperature increase during the exothermic oxidation when air (21% O₂) is employed. A set of three inert gas cycles was initially carried out for all samples in N₂ to investigate the release of oxygen during a span of 360 s. For reactivity test, methane was primarily used for 20 s during reduction cycles and repeated for at least three times. The duration of 20 s was selected as it approximately corresponds to the reduction of CuO to Cu₂O only for CLOU processes. Subsequently, additional cycles were carried out in which the reduction time was increased in steps of 10 s intervals up to 70 s. During the prolonged reduction cycles, it is likely that reduction to Cu is gradually approached, i.e., applicable to CLC. The extended reduction time also helped in evaluating the extent to which the active phase was available.

There was no carbon burnoff during the subsequent oxidation cycles (by way of increase in CO and/or CO₂ concentrations) to show carbon deposition during shorter reduction cycles. This was due to the fact that more oxygen was available than the stoichiometric demand of the fuel. Depending on the oxygen ratio of the respective sample, some carbon

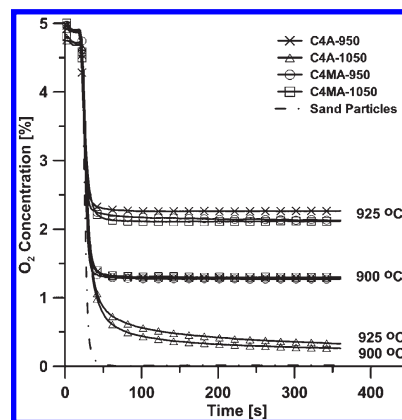


Figure 3. Oxygen concentration of C4A and C4MA oxygen carriers during inert gas cycles at 900 and 925 °C.

was deposited during the extended reduction cycles as they were depleted of oxygen. However, as the deposition of carbon was not frequent, steam was not incorporated.

Nitrogen was used as an inert purge for 60 s in between oxidation and reduction. The exit gas stream from the reactor was led into a condenser to remove the water. The composition and flow rate of the dry gas were determined on a volumetric base by a Rosemount NGA-2000 analyzer which computed the concentrations of O₂, CO₂, CO, CH₄, and H₂. Inlet flow rates of 450, 900, and 600 mL_N/min were used during reduction, oxidation, and inert cycle, respectively. These flow rates were chosen to achieve values ranging between 12 and 17 u_{mf} during oxidation, and between 4 and 6 u_{mf} during reduction, where u_{mf} is the minimum fluidization velocity.²⁷

2.4. Data Analysis. The reactivity of a given oxygen carrier is quantified in terms of gas yield or conversion efficiency (γ), and is defined as the fraction of fully oxidized fuel divided by the carbon-containing gases in outlet stream, in this work CO₂, CO, and CH₄.

$$\gamma_{red} = \frac{x_{CO_2}}{x_{CO_2} + x_{CH_4} + x_{CO}} \quad (5)$$

Here x_i denotes the composition of the respective gas, obtained from measured concentration in the gas analyzer.

The theoretical oxygen capacity of a given carrier is defined in terms of oxygen ratio (R_O), as the maximum mass change of oxygen in the oxygen carrier as follows:

$$R_O = \frac{m_{ox} - m_{red}}{m_{ox}} \quad (6)$$

where m_{ox} and m_{red} are the mass of the oxygen carrier in respectively fully oxidized and reduced state.

Table 2. Phase Analysis of the Oxygen Carriers

		identified phases	
		fresh samples	used samples
C4A-950	CuO, α -Al ₂ O ₃ , CuAl ₂ O ₄ ^a	CuO, α -Al ₂ O ₃ , CuAl ₂ O ₄ , CuAlO ₂	
C4MA-950	CuO, MgAl ₂ O ₄	CuO, MgAl ₂ O ₄	
C4A-1050	CuAl ₂ O ₄ , α -Al ₂ O ₃ , CuO ^a	CuAl ₂ O ₄ , CuAlO ₂ , α -Al ₂ O ₃	
C4MA-1050	CuO, MgAl ₂ O ₄	CuO, MgAl ₂ O ₄	

^a Minor phase.

The conversion of the oxygen carrier, ω , is defined as

$$\omega = \frac{m}{m_{\text{ox}}} \quad (7)$$

where m is the actual mass of the oxygen carrier during the experiments.

Equations 8 and 9 are employed for calculating ω as a function of time during, respectively, reduction and oxidation period from the measured concentrations of various gaseous species in the gas analyzer:

$$\omega_i = \omega_{i-1} - \int_{t_0}^{t_1} \frac{\dot{n}_{\text{out}} M_{\text{O}}}{m_{\text{ox}}} (4x_{\text{CO}_2} + 3x_{\text{CO}} + 2x_{\text{O}_2} - x_{\text{H}_2}) dt \quad (8)$$

$$\omega_i = \omega_{i-1} + \int_{t_0}^{t_1} \frac{2M_{\text{O}}}{m_{\text{ox}}} (\dot{n}_{\text{in}} x_{\text{O}_2, \text{in}} - \dot{n}_{\text{out}} x_{\text{O}_2, \text{out}}) dt \quad (9)$$

ω_i is the instantaneous conversion at time i , ω_{i-1} is the conversion in the preceding instant, and t_0 and t_1 are the initial and final time of measurement. M_{O} is the molar mass of oxygen and \dot{n}_{in} and \dot{n}_{out} are the dry molar flow rates of the gas at inlet and outlet of the reactor, respectively.

3. RESULTS

3.1. Concentration Profiles. Figure 3 shows the oxygen concentration during the inert gas cycle for all samples. During this period, CuO decomposes spontaneously into Cu₂O in the environment of inert nitrogen where the particles release oxygen. The oxygen concentration is relatively consistent with the theoretical equilibrium partial pressure, p_{O_2} , corresponding to the decomposition of CuO into Cu₂O (1.5% and 2.7%, respectively, at 900 and 925 °C⁶). This is true for all the carriers tested in this work with the exception of C4A-1050. The insignificant oxygen released from C4A-1050 (0.2%), is further corroborated by the experiments with sand particles, also included in Figure 3 under identical experimental conditions. As opposed to the C4A-950 particles, the C4A-1050 sample has much less of gaseous oxygen release (CLOU) ability. As seen from Table 1, the only difference between the two materials is the temperature at which they were calcined. Yet, while C4A-950 maintains the anticipated equilibrium oxygen concentration at both operating temperatures, C4A-1050 does only release oxygen to a minor extent. For C4MA-950 and C4MA-1050 samples however, an identical equilibrium concentration of oxygen release is obtained irrespective of the calcination temperature.

Table 2 shows the phase analysis of the fresh and used carriers. The experiments were always ended in the oxidation phase and thus the characterization for the used samples refers to this phase. In the case of the C4A-1050 sample, CuAl₂O₄ is the predominant phase due to the interaction between copper-oxide and alumina caused by the higher calcination temperature at 1050 °C. In the fresh sample, CuO which is capable of releasing oxygen at above 850 °C⁶ appears as a minor phase together with excess and

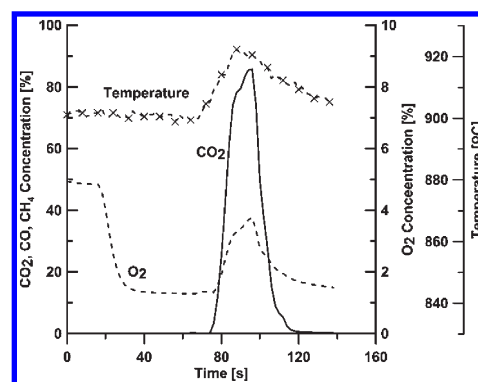


Figure 4. Time-dependent concentration and temperature profile for C4A-950 during reduction cycle at 900 °C.

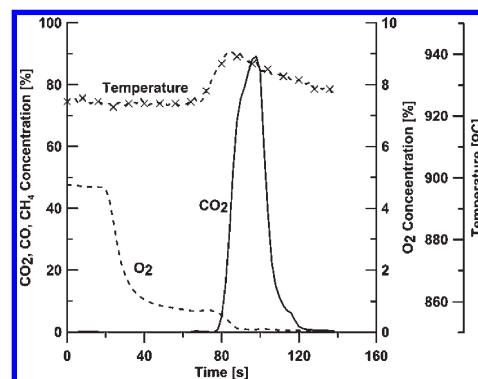


Figure 5. Time-dependent concentration and temperature profile for C4A-1050 during reduction cycle at 925 °C.

unreacted alumina. Thus in this case, very little oxygen is released via the CLOU mechanism since CuAl₂O₄ is quite incapable of releasing oxygen as shown by the phase evolution of the C4A-1050 material described in Section 3.4.

Following the inert gas cycles, successful cycles of oxidation and reduction were carried out for all oxygen carriers. Figure 4 shows the concentration profiles for the C4A-950 sample for the 20 s reduction cycle at 900 °C. The decomposition of CuO during the short interval in inert gas prior to fuel injection is due to the spontaneous release of oxygen via the CLOU mechanism. The fuel (methane) reacts exothermically with the released oxygen, producing CO₂, with concomitant increase in temperature due to the exothermic nature of the reaction; this is common for copper-based oxygen carriers.³ The rise in temperature shifts the thermodynamic equilibria and in turn increases the oxygen concentration. However, the actual oxygen concentration during reduction in the reactor is lower due to dilution created by the water formed. The concentration profiles were similar from cycle to cycle, except for slight variations in peak concentrations due to the transitory nonsteady state. At 925 °C, more oxygen is released during the inert and reduction cycles.

Rather low oxygen release ($\sim 0.2\%$) was seen for the C4A-1050 sample at both 900 and 925 °C (Figure 3), compared to the thermodynamically predicted values for the CuO/Cu₂O buffer at these temperatures (about 1.5% and 2.7%, respectively, at 900 and 925 °C⁶). This was attributed to the lesser availability of CuO (Table 2) due to the interaction with the support. Figure 5 shows the concentration profile of C4A-1050 for the 20 s reduction

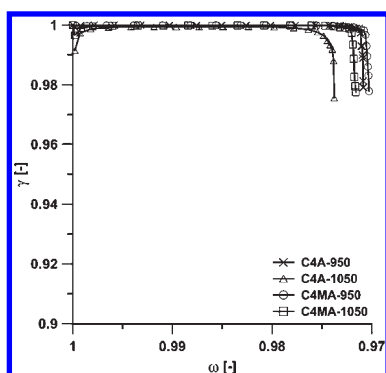


Figure 6. Gas yield, γ , as a function of mass-based conversion, ω , for C4A and C4MA oxygen carriers during 20 s of CH_4 reduction at 925 °C.

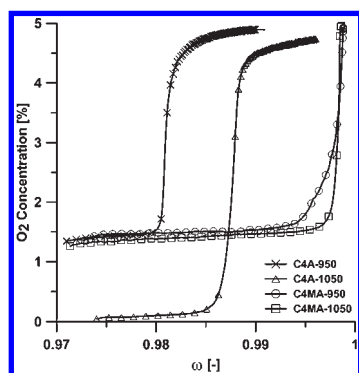


Figure 7. Variation of oxygen concentration with mass-based conversion (ω) during oxidation at 900 °C for C4A and C4MA oxygen carriers.

cycle at 925 °C. It can be seen that the small amount of oxygen released is completely consumed during the reduction phase, confirming also that not much free CuO existed in C4A-1050. For this reason, CuAl_2O_4 which is the major active phase in C4A-1050 does not behave as a CLOU but rather as a CLC material.

The concentration profiles for C4MA-950 and C4MA-1050 samples during 20 s reduction cycles at 900 °C were similar to those shown in Figure 4. Accordingly at 925 °C, more oxygen was released during the inert and reduction cycles. The salient difference between the two profiles was the lower amount of oxygen release for C4MA-950 during reduction.

3.2. Reactivity of Oxygen Carriers. Figure 6 shows the reactivity (in terms of gas yield, γ) of oxygen carriers at 925 °C, using methane as the fuel for the third repeated cycle. The point at which γ plummets indicates the end of 20 s of reduction. As shown, all samples exhibited high reactivity with complete fuel conversion during this period, irrespective of the temperature at which they were calcined (950 vs 1050 °C). The small variation seen in ω value could be due to normal experimental fluctuations, possibly in flow measurements. Similar was the development of γ vs. ω for reactivity tests at 900 °C. The carriers lose approximately 3% of their mass as they are converted during 20 s of reduction (ω going from 1 to 0.97). During the oxidation cycle that follows, the carrier is expected to retrieve this amount of oxygen, meaning that ω must revert from 0.97 to 1. Only then, a truly reversible redox behavior of the carrier could be anticipated.

Figure 7 shows the oxygen partial pressure as a function of oxygen carrier conversion, ω , in the oxidation phase following

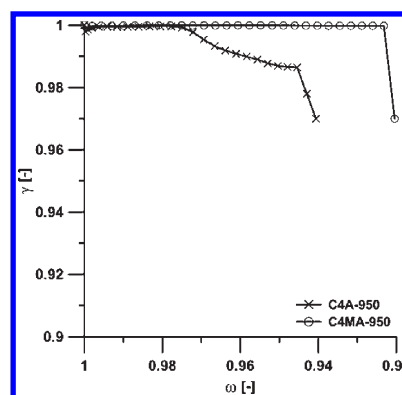


Figure 8. Gas yield (γ) as a function of mass-based conversion (ω) for C4A-950 and C4MA-950 oxygen carriers at 925 °C during 70 s of CH_4 reduction.

the reduction cycle at 900 °C. It can be conceived for C4A-950 that the oxygen partial pressure follows the equilibrium concentration at 1.5% and culminates to 5% while leaving 2% of the oxygen carrier as unconverted as ω proceeds from 0.97 to 0.98. Note that in Figure 6 approximately 3% of C4A-950 was converted during 20 s of reduction with ω extending from 1 to 0.97. Similar is the case for C4A-1050, where ω proceeds from 0.975 to 0.985. The incomplete retrieval of ω in both cases indicates that part of the active phase (respectively CuO and CuAl_2O_4) is lost. However, for the C4MA samples as shown in Figure 7, the carriers retrieved the expected conversion with the value of ω extending to 1 at the equilibrium oxygen concentration for all oxidation cycles and irrespective of the calcination temperature. This shows that the active CuO phase has remained intact when MgAl_2O_4 is used as support.

It is reported that the diffusion of O_2 in the depleted oxygen carrier in the oxidation cycle could be hindered by the CuO layer partially surrounding the reduced Cu_2O and Cu grains.^{25,28,29} Therefore the incomplete oxidation of C4A-950 could initially be connected with this resistance. However, the XRD patterns extracted at the end of experiment for C4A-950 only indicated the oxidized state of the oxygen carrier (i.e., only CuO) together with an increase in the content of CuAl_2O_4 and CuAlO_2 (Table 2). In addition, the C4A-1050 sample which did not contain a significant amount of CuO in the fresh state also could not be completely oxidized. Furthermore, the complete regain of ω in oxidation for the C4MA-950 and C4MA-1050 samples indicates that such resistance in O_2 diffusion is not of concern in the oxygen carriers investigated in this work. Thus as will be shown in the phase analysis later (Section 3.4), the remaining deficiency in ω can be attributed to the fact that a part of the active phase is bound in the form of a ternary compound (CuAlO_2), that is not readily converted back to the initial composition upon oxidation.

Figure 8 shows the gas yield (γ) for the C4A-950 and C4MA-950 samples at 925 °C during the extended reduction cycle (70 s) with methane. Under the experimental conditions employed, the theoretical conversion of CuO to Cu, ω , at the end of reduction should correspond to 0.92. This was nearly obtained in the case of C4MA-950 and in the case of C4MA-1050 particles (not shown) where it reached a value of 0.93 with full conversion of methane. Reduction times longer than 70 s did not increase the conversion any further for either of the two carriers, confirming that the limit of CuO reduction is reached. On the contrary, in

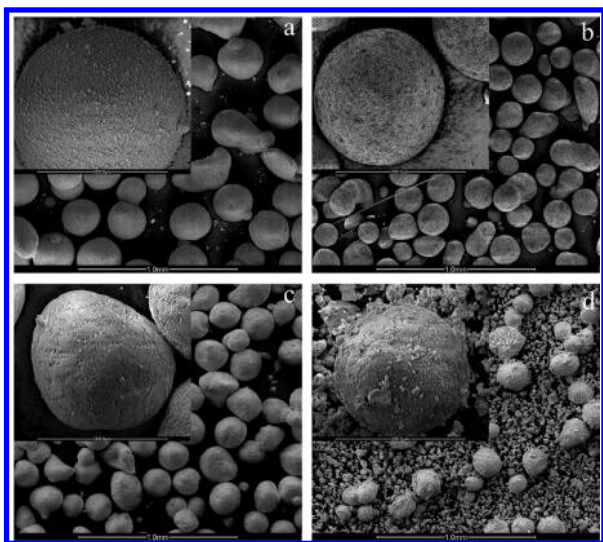


Figure 9. ESEM images of (a) C4A-950, (b) C4A-1050, (c) C4MA-950, and (d) C4MA-1050 after reactivity test.

the case of C4A-950, a maximum value of 0.97 was achieved for ω . This leads to the incomplete conversion of methane during the remainder of the cycle, indicating that not as much CuO was available for reduction.

It should also be pointed out that the final prolonged (70 s) reduction cycle was carried out after 16 cycles from the start of the experiment. Thus the high consistency of the mass-based conversion, ω , with the corresponding theoretical value in the case of C4MA samples indicates that the oxidation of Cu₂O to CuO in previous cycles was not subject to any resistance toward O₂ diffusion in the depleted CuO layer as suggested previously.^{25,28,29} In addition, this shows the intact state of the CuO active phase in these materials.

3.3. Characterization of the Oxygen Carriers. Characterizations of the oxygen carriers were given in Tables 1 and 2. Among fresh samples, it can be observed for the C4A-1050 particles that the apparent density is lower compared to the C4A-950 sample with the BET value almost unchanged. However, it is worth noting that C4A-1050 had essentially a different chemical composition (predominantly CuAl₂O₄) and thus distinct values of apparent density and BET are not unexpected. The BET surface areas of the used samples remained unaltered and did not show any significant variation; the observed small change could be within the experimental error. The postreaction ESEM images of all samples after the reactivity test are shown in Figure 9a–d. Compared to the fresh sample, the used C4A-950 particles exhibited some fragmentation. On the other hand, the surface morphology of the C4A-1050 and C4MA-950 particles did not change appreciably. For the C4MA-1050 sample, most of the particles disintegrated forming considerable amount of debris. The fact that the ESEM micrographs were taken after 17 cycles during which the oxygen carriers were subjected to prolonged reduction indicates that the C4A-1050 and C4MA-950 oxygen carriers have quite promising mechanical resistance.

It is clear that both systems show high reactivity (Figure 6). The MgAl₂O₄-supported carrier has the advantage of no or limited interaction between CuO and the MgAl₂O₄ support. This is true for both oxidizing and reducing experiments in the temperature regime of investigation (Table 2). Thus, from the foregoing set of observations it can be inferred that C4MA-950 is

a suitable oxygen carrier for CLOU processes. This is corroborated by stable and consistent release of oxygen (Figure 3), invariant amount of CuO (Figure 8), and absence of agglomeration and major morphological changes that were seen in the case of C4MA-950 (Figure 9).

The Al₂O₃-supported system is somewhat complicated due to the phase formation probability in the regime of processing as well as application temperatures. The loss of CuO active phase due to formation of CuAlO₂ in C4A-950 (Figure 7 and 8) raises questions about the long-term stability of this oxygen carrier as a CLOU material. On the other hand, C4A-1050 is recognized as a CLC material (Figure 5), though like C4A-950, the active phase (in this case CuAl₂O₄) is not fully obtained upon oxidation (Figure 7). The phase-field shift in the CuO–Al₂O₃ system sheds light on the observed difficulty in the reversible behavior of Al₂O₃-supported CuO oxygen carriers, as discussed below.

3.4. Phase Equilibria Analysis for Al₂O₃-Supported CuO Oxygen Carriers. The relationship among various components in the pseudobinary CuO (Cu₂O)–Al₂O₃ system is of great relevance to CLC and/or CLOU processes concerning the Al₂O₃-supported CuO oxygen carriers. The CuO–Al₂O₃ phase diagram was reported at atmospheric pressure ($p_{\text{O}_2} = 0.21$ atm) by Gadalla and White³⁰ and further developed by Jacob and Alcock.³¹ Based on the method of synthesis (bulk oxide reaction versus thin film formation), considerable disagreements exist as to the accuracy of phase formation and transformation.^{32–36} However, the operative boundaries for the CLC and/or CLOU processes could be defined quite accurately without any ambiguity. For example, irrespective of the modification of the alumina used (such as α , γ , η , or θ , etc.) during material synthesis, the CuAl₂O₄ spinel is invariably formed at high temperatures (above 1000 °C)^{37–39} as per the following solid-state reaction:

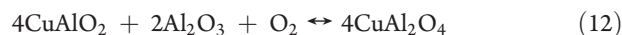


However, the interaction between copper-oxide and γ -Al₂O₃ is much faster and occurs at even much lower temperatures (above 600 °C), compared to that with α -Al₂O₃ owing to large surface area and better reaction kinetics.^{38–40} Thus, in the case of C4A-950, the active phase and support remained individual components and copper(II) aluminate, CuAl₂O₄, was found only as a minor phase in the fresh material, as shown in Table 2.

At around 1026 °C, CuO decomposes into Cu₂O in air, which in turn reacts with free alumina phase to form copper(I) aluminate, delafossite (CuAlO₂):



Between 1050 and 1170 °C in an Al₂O₃-rich mixture, CuAlO₂ is metastable in air and transforms into CuAl₂O₄, via the following reversible reaction:^{38,40,41}



Thus, in the case of C4A-1050, CuAl₂O₄ was formed as the major phase upon calcination at 1050 °C (Table 2). Visual examination of the C4A-950 and C4A-1050 samples also helps in identifying the phases: C4A-950, which consisted mainly of CuO and Al₂O₃, had the appearance of gray to black. On the other hand, C4A-1050 was orange, the color of CuAl₂O₄.⁴²

Annealing of thin copper films deposited on alumina substrates in nitrogen³³ shows that CuAl₂O₄ spinel could be reduced to CuAlO₂ as per reverse of reaction 12. However, as shown in Figure 3, CuAl₂O₄ in C4A-1050 sample does not release oxygen

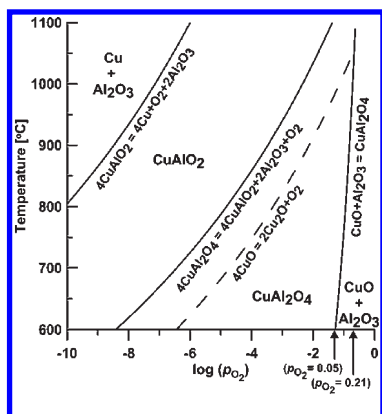


Figure 10. Temperature vs $\log(p_{\text{O}_2})$ diagram in the Cu–Al–O system under 1 atm total pressure.⁴³

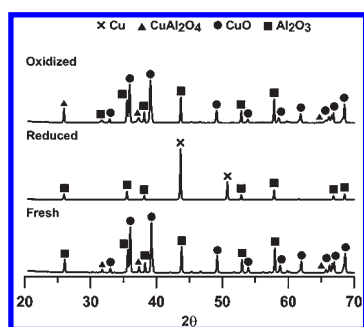
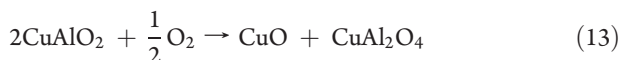


Figure 11. Comparative XRD signatures of fresh, H_2 -reduced, and oxidized (5% O_2 in N_2) samples of C4A-950 at 900 °C.

at a significant level in an inert atmosphere at 900–925 °C. Nonetheless, it can still be reduced by methane as demonstrated in Figure 5 and reported elsewhere using thermogravimetric studies¹⁸ and temperature programmed reduction (TPR).⁴²

Recently, Kumekawa et al.³² reported the T - p_{O_2} boundaries for the CuO – CuAl_2O_4 – CuAlO_2 phase fields. It was shown that CuAlO_2 is thermodynamically stable in air above 900 °C, but that it undergoes the following kinetically hindered decomposition below 900 °C.



In the light of the reaction pathways between CuO and Al_2O_3 and using the Gibbs energy data reported by Gadalla and White³⁰ and Jacob and Alcock³¹ the phase relationships as a function of oxygen partial pressure in the temperature range of relevance could be established. This is shown in Figure 10 after Ingram et al.⁴³ at atmospheric pressure.

According to Figure 10 at $p_{\text{O}_2} = 0.05$ atm, the amount of CuAl_2O_4 (a minor phase in fresh C4A-950) increases by way of reaction 10 with increasing temperature. In case of C4A-950, CuO is amenable to decomposition into Cu_2O under the prevailing conditions of low p_{O_2} at 900 or 925 °C in the fuel reactor and during the inert cycles. This is then likely to promote the reaction with alumina, leading to the formation of CuAlO_2 via reaction 11. In the case of C4A-1050, CuAl_2O_4 is reduced by methane resulting also in the formation of CuAlO_2 . In either case, subsequent oxidation does not readily transform CuAlO_2 into CuAl_2O_4 or CuO via reaction 12 or 13. This is because the

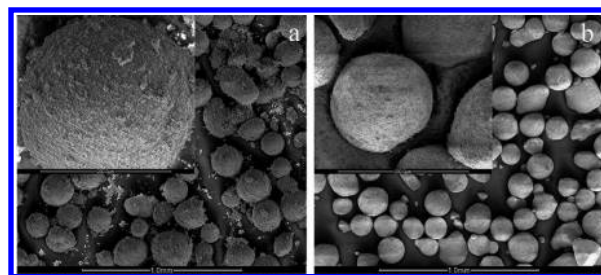


Figure 12. ESEM images of oxidized (a) C4A-950 and (b) C4A-1050 subsequent to full reduction using H_2 . Note the agglomeration in (a) caused by the complete reduction of the oxygen carrier.

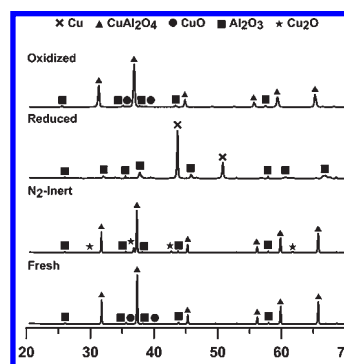


Figure 13. Comparative XRD signatures of fresh, N_2 -inert exposed, H_2 -reduced, and oxidized (5% O_2 in N_2) samples of C4A-1050 at 900 °C.

temperature is lower than required for reaction 12 to proceed and because reaction 13 is kinetically slow as mentioned above. This explains the presence of CuAlO_2 after oxidation for both samples, as evidenced from the XRD analysis in Table 2 and corroborated by Figure 7. It also shows that subsequent to reduction, the carriers were not completely oxidized to the original composition. Thus, the loss of active phase (CuO or CuAl_2O_4) could be related to the formation and increase of the CuAlO_2 phase.

To further investigate the CuO – Al_2O_3 phase equilibria, it was argued that if the reduction were to proceed so as to yield elemental Cu, one could conceivably reclaim the initial composition again upon oxidation without going through the kinetically hindered transformation involving CuAlO_2 . This probability was initially tested by using an independent reduction scheme with H_2 (instead of CH_4) to avoid the formation of coke. The systematic phase evolution in the reduction and oxidation cycles for C4A-950 is shown in Figure 11. The H_2 -reduced sample (Cu and Al_2O_3) could be successfully oxidized to a mixture of CuO and Al_2O_3 , identical to that of the fresh sample. However, there was evidence of agglomeration, as seen from the ESEM images of the oxidized sample shown in Figure 12a.

For C4A-1050, a similar scheme was used. In this case, a long (approximately 4 h) N_2 -inert cycle was used prior to H_2 -reduction. The low release of oxygen from the small amount of CuO (Table 2) as seen in Figure 3 was noticed again, which eventually declined to zero during the long inert period. The reactor was cooled in N_2 and the XRD pattern collected at this extreme indicated the presence of Cu_2O , Al_2O_3 , and CuAl_2O_4 only. The phase analysis of the following H_2 -reduced specimen revealed the presence of Cu and Al_2O_3 . Upon oxidation

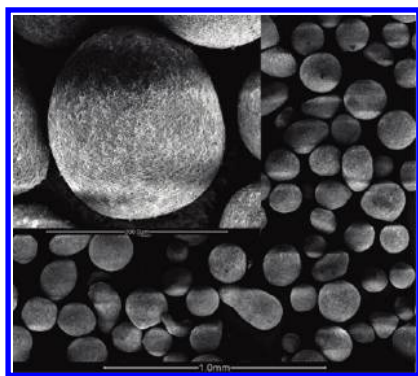


Figure 14. ESEM images of C4A-1050 subjected to multicycle test of full reduction in methane followed by oxidation.

in 5% O₂ stream, a diffraction pattern identical to that of the fresh C4A-1050 sample was obtained (Figure 13). Thus, the carrier was effectively oxidized without going through the kinetically hindered phase transformation involving CuAlO₂ as per reaction 13. Note that at $p_{O_2} = 0.05$ atm, the formation of CuAl₂O₄ from constituent oxides is thermodynamically feasible even at 900 °C (Figure 10).

An attempt was also made to reoxidize the fully reduced C4A-1050 (Cu and Al₂O₃ mixture) in air, assuming that it would oxidize elemental copper fully to CuO (Figure 10). However, the CuAl₂O₄ and Al₂O₃ phase mixture was obtained again. Ertl et al.⁴⁴ observed the formation of CuAl₂O₄ upon oxidation of a Cu and Al₂O₃ mixture at 400 °C in 16% O₂. It was suggested that Cu is initially oxidized to CuO, but the highly disordered and reactive state of CuO and Al₂O₃ particles caused by the redox cycles transforms the mixture into the original spinel even at such low temperatures. For this reason and since reaction 12 is completed at above 1050 °C, at which C4A-1050 was originally calcined, the possible mechanism for the formation of CuAl₂O₄ at 900 °C in both cases ($p_{O_2} = 0.05$ and 0.21 atm) is via reaction 10.

Surprisingly, there was no agglomeration of the bed in either of the oxidation cases for the C4A-1050 sample. The ESEM image of the oxidized C4A-1050 particles is shown in Figure 12b, which shows quite distinct morphological features. The most striking aspect is the extreme smoothness of the particle surfaces, uniformity of the granules, and lack of fine formation in comparison to that observed for C4A-950.

The decomposition of CuAlO₂, though kinetically hindered, can be accelerated if oxidation is carried out in air, i.e., 21% O₂. To illustrate this, oxidation of 5 g of the used C4A-1050 sample (containing considerable amount of CuAlO₂; Table 2) was carried out for about 1¹/₂ h at 900 °C in air. This yielded a mixture of CuAl₂O₄, Al₂O₃ and CuO with the amount of CuO higher (7.5%) compared to the fresh C4A-1050 sample (1.5%) as determined by the XRD; this is in agreement with reaction 13. The color of this sample was chocolate brown due to the increase in CuO content compared to that of fresh C4A-1050 or the one oxidized from fully reduced C4A-1050 (orange), both of which were predominantly composed of CuAl₂O₄. Although in a CLC unit air is used for oxidation, it should be emphasized that the oxygen concentration at the air reactor's outlet is lower, thus part of the CuAlO₂ phase will likely remain from completely decomposing to CuO and CuAl₂O₄.

Table 3. Theoretical Oxygen Ratio of Copper Derivatives

	R _O (%)
CuO/Cu	20.1
Cu ₂ O/Cu	11.2
CuO/Cu ₂ O	10
CuAl ₂ O ₄ /Cu (+Al ₂ O ₃)	8.8

3.5. Agglomeration and Attrition Resistance Attributes of CuAl₂O₄. It was observed that the C4A-1050 sample did not agglomerate when fully reduced and reoxidized. Thus to further evaluate the attrition resistance of CuAl₂O₄, a multicycle test (additional 5 cycles) of C4A-1050, was carried out using methane at 900 °C to simulate a more realistic condition in CLC. Neither agglomeration nor defluidization was encountered. It was possible to completely reduce the oxygen carrier in methane and fully oxidize it in 5% O₂ in a manner similar to that shown in Figure 13. This negates the concern over the possibility of reducing CuAl₂O₄ to Cu and Al₂O₃ using methane as fuel. The ESEM analyses on the C4A-1050 subjected to the multicycle test are shown in Figure 14; any sign of agglomeration or the presence of fines are absent.

In light of this, the use of CuAl₂O₄ can be suggested for CLC processes due to agglomeration and attrition resistance of this oxygen carrier. The oxygen ratio for various phases in the Cu–Al–O system is shown in Table 3. It was previously found that employing a low amount of CuO (less than 20 wt%) by impregnation in Al₂O₃ helps to avoid agglomeration.¹⁰ In such case, the oxygen ratio would be lower than pure CuAl₂O₄, given its higher copper content.

4. CONCLUSION

The conclusions drawn from this work are as follows. For Al₂O₃-supported CuO oxygen carriers calcined at 950 and 1050 °C, it is inferred from analysis of the phase equilibria at above 900 °C that

- (1) Part of the active phase (respectively CuO and CuAl₂O₄) is bound as CuAlO₂ during incomplete reduction with slow kinetics for reoxidation. This results in partial loss of the active phase after several redox cycles.
- (2) If complete reduction is attained, the original active phase composition can be rejuvenated. In this case, the use of CuAl₂O₄ as an oxygen carrier can be suggested for CLC processes due to resistance against agglomeration and attrition. Moreover, CuAl₂O₄ spinel has a higher oxygen transport capacity than low-CuO loading on Al₂O₃ support oxygen carriers.

For MgAl₂O₄-supported CuO oxygen carriers, it is concluded that the active CuO phase is retained by avoiding the interaction between CuO and Al₂O₃ thus offering a stable oxygen release capacity due to existence of relatively intact CuO. Together with the absence of major morphological changes, the MgAl₂O₄-supported CuO appears as a suitable oxygen carrier for CLOU processes, although long-term validation of their use with solid fuels and in continuous operation is needed.

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