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Innovative Oxygen Carrier Materials for Chemical-Looping Combustion

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Abstract

In chemical-looping combustion, the oxygen needed for combustion of fuel is provided by metal oxides called oxygen carriers, and inherent separation of CO_2 is achieved without energy penalty. For gaseous fuels, such as natural gas, Ni-based oxygen carriers have generally been shown to be the most reactive. But as Ni-based materials are burdened by high costs and environmental risks with respect to toxicity, it is of high importance to find viable non-Ni alternatives. In the EU-financed project INNOCUOUS, one of the key issues is to find novel non-Ni based oxygen carriers. In this paper results from reactivity investigations of three groups of oxygen carrier materials are reported. The materials were prepared by spray-drying, and are based on 1) CuO, 2) Ca-Mn-X-O where X=Cu, Fe, Ti and Mg, and 3) Mg-Mn-O. A number of materials showed a combination of sufficient mechanical strength, high release of gas phase oxygen and high reactivity with methane, and can thus be considered viable alternatives to Ni-based materials.

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Keywords: Chemical-looping Combustion; Oxygen carriers; Spray-drying; Methane; Fluidized bed

1. Introduction

Chemical-looping combustion (CLC) is a two-step combustion technology in which a solid oxygen carrier is used to transfer the oxygen required for combustion from an air reactor to a fuel reactor, thus preventing direct contact between air and fuel. The combustion air and fuel reacts with the metal oxide particles according to the overall reactions,

Fuel reactor: $CH_4\,(CO, H_2) + MeO \rightarrow CO_2 + H_2O\,(CO_2, H_2O) + Me$ (1)

Air reactor: $Me + \frac{1}{2}O_2 \rightarrow MeO$ (2)

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The total amount of heat evolved from reaction (1) plus (2) is the same as for normal combustion where the oxygen is in direct contact with the fuel. The advantage with this approach compared to normal combustion is that the CO_2 is inherently obtained in a highly concentrated CO_2 stream ready for sequestration and there are no costs or energy penalties for gas separation[1]. CLC uses well-established boiler technology very similar to circulating fluidized bed boilers. Thus, CLC could play a significant role in achieving large reductions in emissions of CO_2 and hence combating global warming.

The oxygen carrier is vital for the implementation of the CLC process. Suitable thermodynamic and kinetic properties are required for it to be operationally feasible and capable of achieving high CO_2 capture efficiency. Sufficient mechanical strength, stability and durability are also desired[2].

Recently, some oxygen carriers have been developed which can release oxygen directly in gas phase, see Ryden et al. for an overview[3]. This concept is referred to as chemical-looping with oxygen uncoupling (CLOU). The oxygen release from a CLOU material occurs through reaction (3). It is believed that the fuel conversion can be substantially improved using CLOU materials, because direct reaction between fuel and gaseous oxygen requires less perfect mixing than gas-solid reactions.

$$Me_xO_y \rightarrow Me_xO_{y-2} + O_2 \quad (3)$$

In an earlier EU-financed project, chemical-looping combustion with natural gas was taken to a unprecedented level of achievement by operating the process with a Ni-based oxygen carrier for over 1000 h in a 10 kW natural gas fired unit, as well as demonstration it in a 120 kW unit[4, 5]. However, due to the toxicity and high cost of Ni, it would be desirable to find non-Ni based oxygen carriers which have similar, or better, characteristics than Ni-based material with respect to reactivity and lifetime.

This paper presents results from the first part of a 3-year project, INNOCUOUS, devoted to advancing the CLC technology with gaseous fuels. One significant part of the project is to develop new and innovative oxygen carriers which contain no or very little Ni. The project is on-going and part of the EU's Seventh Framework programme, with support from the CCP (Carbon Capture Project). In the first part of the project, a substantial number of oxygen carriers have been produced with spray-drying and investigated with respect to parameters important for CLC operation, such as reactivity, strength and defluidization/agglomeration behavior.

At Chalmers University of Technology focus has been on developing materials with CLOU properties. Both CuO, which has substantial and well known oxygen uncoupling characteristics, as well as several combined oxides, have been developed and tested within the project. In this paper, results from testing of several types of CuO-materials as well as combined oxides of Ca-Mn-X-O and Mg-Mn-O will be reported upon. Results from the entire screening of oxygen carriers within the project will be reported upon in a follow-up publication.

2. Experimental

Oxygen carriers in this work were produced by VITO using the commercial spray-drying method. This industrial process can produce highly spherical, free-flowing and homogeneous on the micro-scale oxygen-carrier particles. Raw materials and organic additives were weighed and suspended in deionised water prior to homogenization. The water based suspension was atomized to small droplets which were sprayed into a hot drying medium, normally hot air. The large surface-to-volume ratio of the droplets allows rapid water evaporation and the resulting dry powder is separated from the hot air. After spray drying, synthesized particles were sieved and sintered at different temperatures with a dwelling time of 4 h at the set-point temperature. Sintering temperature and other detailed information are included in Table 1, Table 2 and Table 3 for the three groups of materials respectively.

After sintering, particles with diameter 180-212 μm were selected for crushing strength (CS) measurement. A Shimpo FGN-5 apparatus was used to measure the force needed to fracture a single particle. The numerical average value of 30 particles was calculated as the CS for the sample.

For the reactivity testing, a sample of 15 g of oxygen carrier with diameter 125-180 μm was placed on a porous plate locating 370 mm from the bottom of an 870 mm in length, 22 mm in inner diameter quartz fluidized-bed reactor for reactivity test. Thermocouples were placed 25 mm above and 5 mm below the porous plate to measure the temperature over the bed. Over bed pressure drop was measured at 20 Hz using pressure transducers. The bed material was heated under 5% O_2 (diluted in N_2, 900 mL_N/min) to a set-point temperature, after which cyclic experiments were initiated. In this paper, CLOU experiments were performed at 925°C for CuO-materials and 900°C for Ca-Mn-X-O materials and Mg-Mn-O materials. When the temperature was stable, particles were exposed to N_2 (600 mL_N/min) for 360s and 5% O_2 alternatively for 3 cycles for determination of the uncoupling properties of the material. This is because when the oxygen is removed in the bypassing gas there will be driving force for oxygen release, which can be gauged by measurement of the oxygen concentration. After oxidation of bed materials, the experimental temperature was adjusted to fuel reactivity test condition, which was 925°C for CuO-based materials and 950°C for the rest of materials. Particles were exposed alternatively to 450 mL_N/min CH_4 for 20 s and 900 mL_N/min 5% O_2 until fully oxidized for 3 times. Before and after fuel injection, N_2 (600 mL_N/min) was used to flush the reactor for 60 s to prevent back mixing of inlet oxygen and methane. The flue gases after steam condensation were led through Rosemount NGA-2000 gas analyzer where the concentrations of O_2, CO, CO_2, CH_4 as well as volumetric flow were measured.

In order to evaluate the oxygen carrier reactivity towards methane, the methane conversion was defined as a degree of how much injected methane was fully converted into CO_2 shown as equation (4), where p_i is the outlet partial pressure of component i. The conversion of oxygen carrier (or solid conversion) was defined as equation (5) where m is the mass of the oxygen carrier and m_{ox} is the mass of the fully oxidized oxygen carrier.

$$\gamma_{CH4} = \frac{p_{CO_2}}{p_{CO_2} + p_{CO} + p_{CH4}} \quad (4) \qquad \omega = \frac{m}{m_{ox}} \quad (5)$$

The mass based conversion of the oxygen carrier,ω, can also be integrated for time interval i, as equation (6), when used fuel was methane. To simplify the comparison between particles, a key value for γ is calculated which is a weighted average γ_{CH4} over a certain interval of ω. In this case, ω is between 1 and 0.98 for CuO-based materials and 0.99 for the other types of materials. In some cases the gas conversion was calculated for the 20 s reduction period, as specified in the text.

$$\omega_i = \omega_{i-1} - \int_{t_0}^{t_1} \frac{1}{n_0 p_{out}} \dot{n}_{out}(4p_{CO_2,out} + 3p_{CO,out} - p_{H_2,out}) \quad (6)$$

3. Results and discussion

3.1. CuO-based materials

CuO is the most commonly investigated CLOU material, primarily due to the high rate of oxygen release[6]. However, there has not been any published CLOU experiments in continuous units with CuO using gaseous fuels, and hence there is a need for development of this type of oxygen carriers. Here, 14 kinds of CuO-based materials were spray-dried with different support materials. Selected support materials were ZrO_2 -based, CeO_2 -based, $MgAl_2O_4$ and Fe-based materials. The weight percentage of active phase CuO was set as 20%, 36%, 40% or 60%. As summarized in Table 1, some of the oxygen

carriers had a low mechanical strength, with a CS less than 1 N. Also, during the reactivity tests, some materials showed defluidization problem during experiment. No reactivity data was obtained for these materials. In Table 1, these oxygen carriers are indicated by showing the sintering temperature in italics and underlined.

For those particles where experiments were successfully carried out, the results were very promising. About 2% uncoupled oxygen was detected at the end of 360 s inert cycles at 925°C for all oxygen carriers, the exception being the Cu36FeAl24, which showed lower uncoupling properties. This could be due to the fact that no free CuO was available in these particles. It should be noted that the equilibrium O_2 concentration at this temperature is 2.7%[7]. The materials reactivity towards methane was also very high at 925°C. Full methane conversions were achieved for 7 of 10 oxygen carriers. The lowest average methane conversion was given by Cu36FeAl24, and was 83%. The oxygen concentration profiles and methane conversion as a function of solid conversion can be found in figure 1 and 2.

Table 1.Summary of crushing strength, CLOU properties and reactivities towards methane of CuO-based materials

Notation[1,2]	Sintering temp. (*°C*)[3]	Crushing str. (*N*)[3]	Concentration of uncoupled O_2 at T=925°C (*%*)[4]	γ_{CH4} at T = 925°C[5]
Cu20Z	*1000*	*1.35*	---	---
Cu40Z	950, *1100*	3.41, *4.53*	1.78, ---	1, ---
Cu40ZLa5	950, *1100*	1.39, *1.26*	1.95, ---	1, ---
Cu40(YSZ)	*1000*,1100	*0.42*, 0.56	---, 2.1	---, 1
Cu20Ce	*1000,1100*	*0.83, 0.90*	---, ---	---, ---
Cu40Ce	950, *1100*	0.98, *1.53*	1.70, ---	1, ---
Cu40CeLa5	950*, 1100*	*0.30, 1.26*	---, ---	---, ---
Cu40(MgAl)	*950*, 1100	*0.35*, 0.88	---, 1.71	---, 1
Cu40(MgAl*)[6]	*950*,1100	*0.63*, 1.40	---, 1.87	---, 1
Cu40(MgAl)La5	*950*, 1100	*0.44*, 0.53	---, 1.95	---, 1
Cu60F	950, *1100*	1.00, ---	2.72, ---	0.90, ---
Cu40MF41	*950, 1100*	*1.29, ---*	---, ---	---, ---
Cu40MgF48	950, *1100*	0.95, ---	1.87, ---	0.86, ---
Cu36FAl24	*950*, 1100	*0.37*, 1.18	---, 0.30	---, 0.83

Note: 1. Cu=CuO, Z=ZrO_2, La=La_2O_3, YSZ=Y_2O_3 stabilized ZrO_2, Ce=CeO_2, MgAl=$MgAl_2O_4$, F=Fe_2O_3, M=Mn_3O_4, Mg=MgO. 2. The number after an element suggests the weight percentage of the raw material in synthesis recipe. 3. Italic and underline marked samples indicates that reactivity data was not obtained due to low crushing strength and/or defluidization problem or failure in manufacture 4. Concentration of uncoupled O_2 was taken at the end of a 360 s inert cycle. 5. γ_{CH4} was calculated either for $\Delta\omega$=0.02 or 20 s if $\Delta\omega$ was not below 0.02 at the end of a reduction cycle. 6. MgAl* is a finer and more expensive $MgAl_2O_4$ than the one MgAl represents.

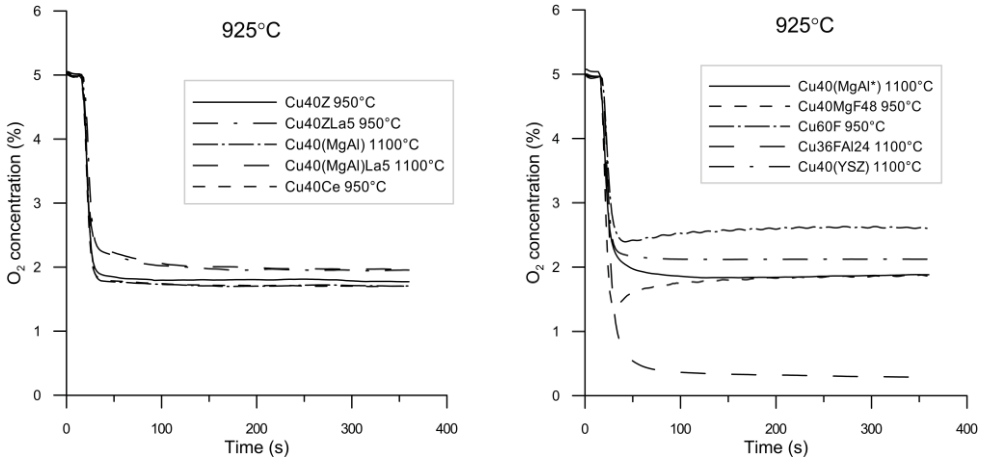

Fig. 1. The O_2 concentration profile of the 2nd inert cycles performed at 925°C for CuO-based materials

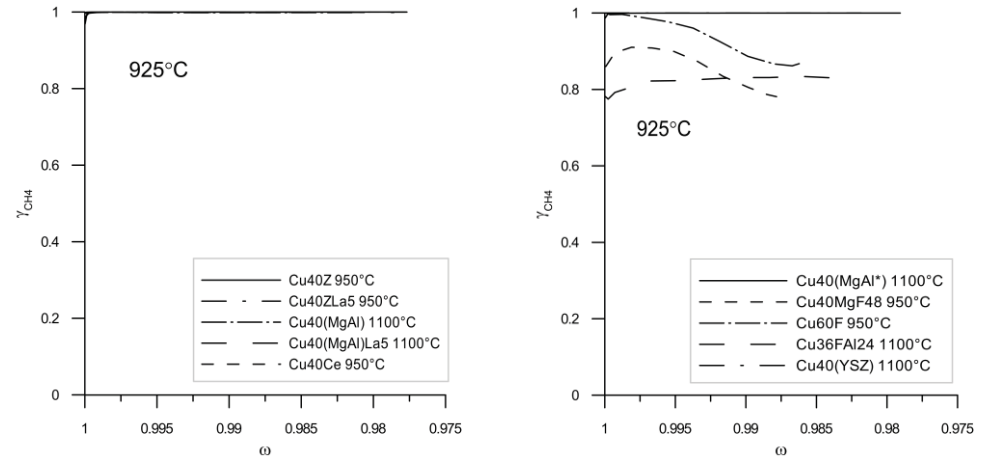

Fig. 2. Methane conversion vs. solid conversion for 2nd methane cycles at 925°C performed on CuO-based materials.

3.2. Ca-Mn-X-O, where X=Cu, Fe, Ti and Mg

In this system of oxygen carriers, shown in Table 2, materials with a $Ca(OH)_2$ around 50 wt% were designed to yield the $ABO_{3-\delta}$ perovskite type structure, where A=Ca, B=Mn in this work, and are indicated by P in brackets in the table. By adding additives Cu, Fe, Ti and Mg, the B-site was partly substitutes, thus creating oxygen deficiency δ due to the different oxidation states between the substitute and Mn. Such $ABO_{3-\delta}$ structure was reported to have CLOU effect and good stability since there is no phase change between the oxidation and reduction state[8, 9]. Several additives with varied amount were studied and the results were presented in Table 2. The idea behind the rest of the materials was to examine different ratios of Ca:Mn:Fe:Mg. Generally, materials with $Ca(OH)_2$ less than 49% in raw materials did not work well. They either had poor fluidization properties or low conversion of methane at 950°C. For the perovskite materials, low crushing strength or fluidization problem was observed for samples containing Cu. The ones with Fe, Ti or Mg additive exhibited oxygen uncoupling abilities at

900°C and high methane conversion at 950°C. Figure 3 shows the oxygen concentration profile of the 2nd inert cycles and the methane conversion as a function of the mass based oxygen carrier conversion of the 2nd fuel cycle for materials of perovskite structure where good fluidization was established.

Table 2.Summary of crushing strength, CLOU properties and reactivity towards methane of Ca-Mn-X-O based materials

Notation[1]	Sintering temp. (°C)	Crushing str. (N)	Concentration of uncoupled O_2 at T=900°C (%)	γ_{CH4} at T = 950°C[2]
C16MF17	1200, 1300	1.38, 2.14	0, 0	0.39, 0.11
C16MF46	*1200*	2.41	0.13	---
C19MMg21	*1200, 1300*	*0.18, 0.27*	---, ---	---, ---
C24MF13	*1200,* 1300	*0.58,* 1.00	---, 0.12	---, 0.45
C24MF35	*1200*	1.94	0.08	---
C28MMg15	*1200, 1300*	*---, ---*	---, ---	---, ---
C30MZ40Mg2	*1200,* 1300	*0.45,* 1.43	---, 0	---, 0.37
C32MF23	*1200, 1300*	*1.71, 3.03*	0.31, 0.28	---, <0.21
C33MF9	*1200, 1300*	*0.22, 0.60*	---, ---	---, ---
C36MMg10	*1200, 1300*	*0.21, 0.23*	---, ---	---, ---
C49MCu5(P)	*950, 1100*	*0.57, 1.25*	---, ---	---, ---
C49MCu5F5(P)	*950, 1100*	*0.33, 1.07*	---, ---	---, ---
C49MCu11(P)	*950, 1100*	*0.50, 1.17*	---, ---	---, ---
C49MCu26(P)	*950, 1100*	*0.46, 0.62*	---, ---	---, ---
C49MF5(P)	*1100,* 1200, 1300	*0.4,* 0.97, 1.38	---, 0.46, 0.48	---, 0.98, 0.92
C49MF11(P)	*1100,* 1200, 1300	*0.39,* 1.11, 1.43	---, 0.47, 0.50	---, 0.93, 0.87
C49MT3(P)	*1100, 1200,* 1300	*0.46, 0.68,* 1.29	---, ---, 0.56	---, ---, 0.94
C49MT13(P)	*1100, 1200,* 1300	*0.46, 0.63,* 1.30	---, ---, 0.37	---, ---, 0.86
C50MT7Mg3(P)	1300, 1350	1.39, 2.44	0.41, 0.42	0.94, 0.93
C51MMg3(P)	*1100, 1200,* 1300	*0.27, 0.56,* 1.38	---, ---, 0.46	---, ---, 0.98
C52MMg6(P)	*1100, 1200,* 1300	*0.36, 0.65,* 1.28	---, ---, 0.38	---, ---, 0.99

Note: 1. C=$Ca(OH)_2$, M=Mn_3O_4, F=Fe_2O_3, Mg=MgO, Z=ZrO_2,Cu=CuO, T=TiO_2 2. γ_{CH4} was calculated either for $\Delta\omega$=0.01 or 20 s if $\Delta\omega$ was not below 0.01 at the end of a reduction cycle. Refer to Table 1 note for non-clarified parameters.

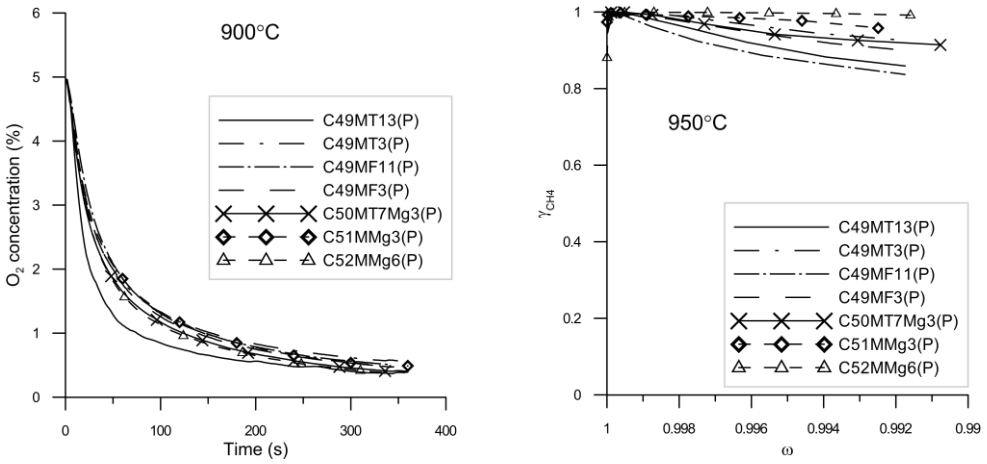

Fig. 3. O_2 concentration profile of the 2nd inert cycles performed at 900°C (left) and methane conversion vs. solid conversion of the 2nd methane cycles at 950°C (right) for 1300°C sintered Ca-Mn-X-O materials. Highly reactive materials were selected here. Data for the rest are shown in Table 2.

3.3. Mg-Mn-O

It has been reported that the combined oxide system based on the Mn-Mg-O can have interesting CLOU properties[3]. However, very little experimental work has been done on the system, the exception being the work performed by Shulman et al[10]. With the aim of forming viable CLOU material, a few Mg-Mn-O materials were spray-dried and investigated in the batch fluidized-bed system. Three synthesized compositions were selected where the weight percentage of MgO in raw materials was 21%, 26% and 35% respectively. In Table 3 and Figure 4, it can be seen the best results were achieved with the highest MgO content samples MMg35. At 900°C, CLOU properties were detected on samples sintered at both 1200°C and 1300°C which had an oxygen concentration of 0.6% and 0.33% after 360 s in inert gas, the average methane yield was 84% and 65% respectively.

Table 3.Summary of crushing strength, CLOU properties and reactivity towards methane of Mg-Mn-O materials

Notation[1]	Sintering temp. (°C)	Crushing str. (*N*)	Concentration of uncoupled O_2 at T=900°C (%)	γ_{CH4} at T = 950°C[2]
MMg21	1200, 1300	2.51, 4.28	0.00, 0.00	0.65, 0.46
MMg26	1200, 1300	2.52, 3.41	0.01, 0.00	0.70, 0.62
MMg35	1200, 1300	1.38, 3.38	0.60, 0.33	0.84, 0.65

Note: 1. M=Mn_3O_4, Mg=MgO. 2. γ_{CH4} was calculated either for $\Delta\omega$=0.01 or 20 s if $\Delta\omega$ was not below 0.01 at the end of a reduction cycle. Refer to Table 1 note for non-clarified parameters.

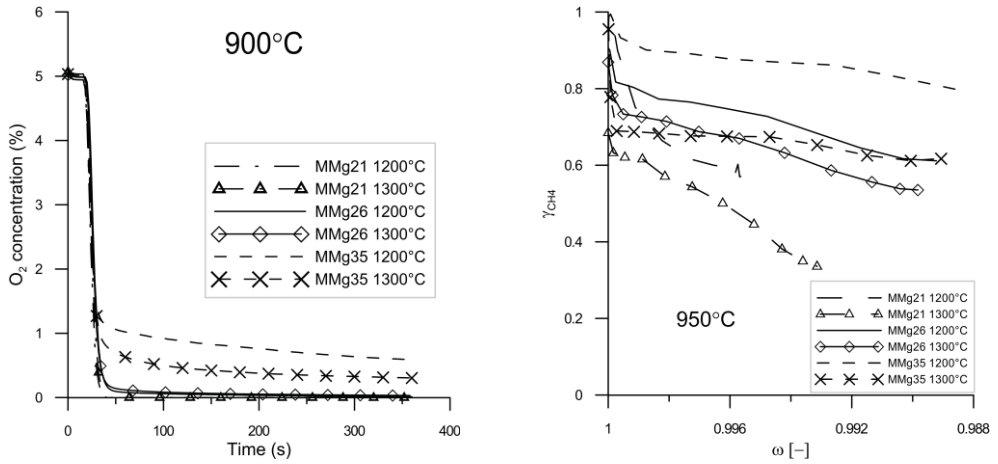

Fig. 4. O_2 concentration profile of the 2nd inert cycles performed at 900°C (left) and methane conversion vs. solid conversion of the 2nd methane cycles at 950°C (right) for 1300°C sintered Mg-Mn-O materials.

4. Conclusion

In the EU-financed INNOCUOUS project, a large number of non-Ni oxygen carriers have been prepared with spray drying and examined with respect to CLC with natural gas. In this paper, three groups of innovative oxygen carriers were produced by spray-drying and examined in a batch fluidized-bed reactor system. Key characteristics of the materials such as reactivity, crushing strength and defluidization behavior are reported. Most of the supported CuO materials provided full methane conversion at 925°C and released around 2% gaseous oxygen at the end of 360 s inert cycle. For the Ca-Mn-X-O system, materials which were formulated to obtain the $CaMnXO_{3-\delta}$ perovskite structure yielded promising results, the exception being the material which included Cu. Also one Mg-Mn-O material showed promise as an oxygen carrier, with reasonable uncoupling properties and an average γ_{CH4} of 84% at the conditions utilized here.

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