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Yilmaz, D., Darwish, E., Leion, H. (2021). Utilization of promising calcium manganite oxygen carriers for potential thermochemical energy storage application. *Industrial & Engineering Chemistry Research*, 60(3): 1250-1258.
<http://dx.doi.org/10.1021/acs.iecr.0c05182>

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Utilization of Promising Calcium Manganite Oxygen Carriers for Potential Thermochemical Energy Storage Application

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Cite This: *Ind. Eng. Chem. Res.* 2021, 60, 1250–1258

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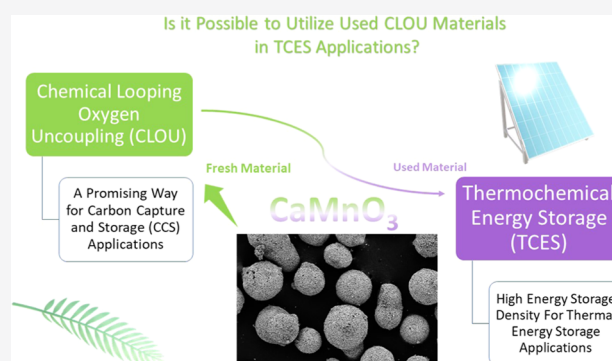
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ABSTRACT: In this study, oxygen release/consumption behavior of calcium manganese-based oxides ($\text{CaMn}_{1-x}\text{B}_x\text{O}_3$, where B: Cu, Fe, Mg and $x = 0.1$ or 0.2) used in a chemical looping oxygen uncoupling (CLOU) application was investigated. The effect of B-site dopants such as Fe, Mg, and Cu on the oxygen release behavior was also investigated with the aim to use these materials in thermal energy storage (TES). Previous literature studies about CLOU performance of doped calcium manganites were taken into consideration for dopants selection. Calcium manganite-based oxides have been used in chemical looping oxygen uncoupling (CLOU) applications owing to their oxygen release behavior to the gas phase. Studies have revealed that calcium manganite-based oxides show a promising nonstoichiometry over a range of temperatures and oxygen partial pressures, which makes them useful for thermochemical energy storage applications. However, the related literature studies have been mainly focused on their nonstoichiometric characteristics related to temperature and oxygen partial pressure and thermodynamic properties. In this work, thermal analysis and fluidized bed tests were carried out as complementary techniques. $\text{CaMn}_{0.8}\text{Cu}_{0.2}\text{O}_3$ showed the highest oxygen release performance in fluidized bed tests, while $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_3$ had the best cyclic stability overall among the samples used in the study.



INTRODUCTION

Thermal energy storage (TES) is a necessary tool to reach the sustainable energy goals via green and sustainable energy resources.¹ Continuous electricity production is important, and it only becomes possible with storing the energy during on-sun hours and releasing the stored energy during off-sun hours.² Among the energy storage techniques, thermochemical energy storage (TCES) exhibits a significantly good performance regarding energy storage density (0.5–1 kWh/kg),³ theoretically unlimited storage period or storage within a large temperature range (25–1000 °C).⁴ Besides, there is no need to use specific and complex storage procedures as the heat is stored in the form of chemical energy in TCES.⁵ To store a high amount of energy, redox reactions of metal oxides can be useful since their operational temperatures are relatively high.⁶ From metal oxides, Co_3O_4 , CuO , Fe_2O_3 , and Mn_2O_3 show remarkable performance to meet the expectations for TCES applications.⁷ Among these oxides, Mn_2O_3 is very promising since it is less expensive, more abundant, more cyclically stable, and environmentally friendly.^{8,9} Since the reoxidation rates of pure Mn_3O_4 to Mn_2O_3 are slightly slow, the combination of the Mn oxides was also tested in some studies to increase the performance of the Mn oxides for thermochemical energy storage applications.^{4,10–15} Especially, Cu/Mn combined oxides showed a lower redox temperature than the pure Cu or Mn oxides.^{4,16} In addition, Fe/Mn combined oxides also

showed much faster reoxidation rates compared to pure Mn oxides.^{10,13,16}

In the literature, there are a few studies about CaMnO_3 as a thermochemical energy storage material.^{17,18} These studies were focused on redox characteristics, redox chemistry, and oxygen nonstoichiometry of the material.^{17–20} However, there is no available systematic study about the effect of dopants on the oxygen release behavior of CaMnO_3 so far.

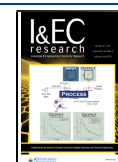
However, Mn-based systems require performance improvement as they feature slow kinetics of the oxidation step.¹⁴ Slow kinetics of Mn-based system have also been seen in chemical looping oxygen uncoupling applications.²¹ To tackle this problem in chemical looping oxygen uncoupling (CLOU), Mn oxides have been combined with other oxides such as SiO_2 , Fe_2O_3 , MgO , and CaO .^{22–24} Especially calcium manganese-based materials have shown great promise as the reactivity is high and estimated lifetime is long enough to be used in chemical looping oxygen uncoupling (CLOU) applica-

Received: October 23, 2020

Revised: January 5, 2021

Accepted: January 5, 2021

Published: January 13, 2021



tions.^{25–27} Calcium manganite, $\text{CaMnO}_{3-\delta}$, has a perovskite-type structure and shows continuous nonstoichiometry with respect to oxygen.¹⁷ The δ -factor defines the degree of oxygen deficiency in the structure.^{19,28} This characteristic enhances the oxygen mobility in the lattice, and it can release oxygen to the gas phase over a range of temperatures.²⁹ These features raise CaMnO_3 to be a perfect fit as a thermochemical energy storage material.

In this study, doped calcium manganite-based oxygen carriers used in methane reactivity tests²⁹ were investigated as potential thermochemical energy storage materials. The effects of dopants such as Cu, Fe, and Mg on the oxygen release behavior of CaMnO_3 were investigated systematically. The amount of dopant (A) was kept as $x = 0.1$ or 0.2 where the sample composition was $\text{CaMn}_{1-x}\text{A}_x\text{O}_3$ (A: Fe, Mg, Cu). The effect of dopant combination such as Cu–Fe and Mg–Ti was also investigated.

EXPERIMENTAL SECTION

The oxygen carriers used in this study were produced by VITO (Flemish Institute for Technological Research) by the spray-drying method, and the materials were designed to have a molar composition of $\text{CaMn}_{1-x}\text{A}_x\text{O}_3$ (A: Fe, Mg, Cu, Cu&Fe, Mg&Ti). The detailed synthesis conditions and the parameters related to the chemical looping oxygen uncoupling application, where the chosen calcium manganates were used as oxygen carriers, can be found elsewhere.²⁹ The starting chemical compositions of the powders are given in Table 1. The phase

Table 1. Designed Chemical Composition and Notation of Samples Used in This Study^a

sample ^{ref work}	composition
CM ³⁰	CaMnO_3
CMF1 ³¹	$\text{CaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$
CMF2 ³¹	$\text{CaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$
CMM1 ^{26,29,32}	$\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_3$
CMM2 ^{29,32}	$\text{CaMn}_{0.9}\text{Mg}_{0.2}\text{O}_3$
CMC1	$\text{CaMn}_{0.9}\text{Cu}_{0.1}\text{O}_3$
CMC2	$\text{CaMn}_{0.9}\text{Cu}_{0.2}\text{O}_3$
CMCF	$\text{CaMn}_{0.8}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{O}_3$
CMMT ^{26,33}	$\text{CaMn}_{0.775}\text{Mg}_{0.1}\text{Ti}_{0.125}\text{O}_3$

^aReference work (ref work) refers to the published results with using the same composition in a CLOU operation.

analysis of the samples after having been used in CLOU applications (called fresh) and after the fluidized bed tests (called used) is given in the Supporting Information. The samples after having been used in CLOU applications were sieved into the 180–250 μm size range to get rid of possible destroyed particles.

Characterization of the synthesized samples for phase analysis was done using an X-ray diffractometer (XRD, Bruker D8 Advance, Cu $K\alpha$, 40 kV, 40 mA) in the 2θ range of 20–75° with a step size of 0.01. Phase analysis was conducted on samples before and after being used in the cyclic experiments. A scanning electron microscope (SEM, Zeiss LEO Ultra 55 FEG) was used to study the particle morphologies. Detailed information is given in the Supporting Information. For thermal analysis, a simultaneous thermal analyzer (STA)-(Netzsch-STA 409 PC Luxx) was used to determine thermal behavior. For each experiment, the amount of sample was 70 mg. The samples were exposed to air and N_2 during all

oxidation cycles ($p\text{O}_2$: 0.21 atm) and reduction cycles, respectively. To study the oxygen release/consumption behavior of the perovskites, several redox cycles including heating and cooling steps were carried out in a fluidized bed reactor with a length of 820 mm and a porous quartz plate of diameter 22 mm placed 370 mm from the bottom. For each experiment, the amount of sample was 15 g. The reduction and oxidation cycles were initiated by changing the temperature between 600 and 1000 °C for each cycle. The system was flushed by air ($p\text{O}_2$: 0.21 atm) during the oxidation cycles and by N_2 during the reduction cycles. The O_2 level in the outlet gas was detected by a Rosemount NGA 2000 multicomponent gas analyzer.

RESULTS

To understand the redox characteristics of the doped calcium manganites used in this study, the properties of the pure calcium manganite were also investigated. The CaMnO_3 system was chosen as it showed good performance as an oxygen carrier in a chemical looping oxygen uncoupling study.³⁴ In the literature, thermochemical energy storage experiments are mainly carried out with either thermal analysis setups or packed bed reactors.^{6,35} In this study, the redox characteristics of the samples were investigated via both thermal analysis and fluidized bed experiments.

Figure 1a,b shows the thermal behavior of CM under controlled atmosphere and the oxygen release/consumption

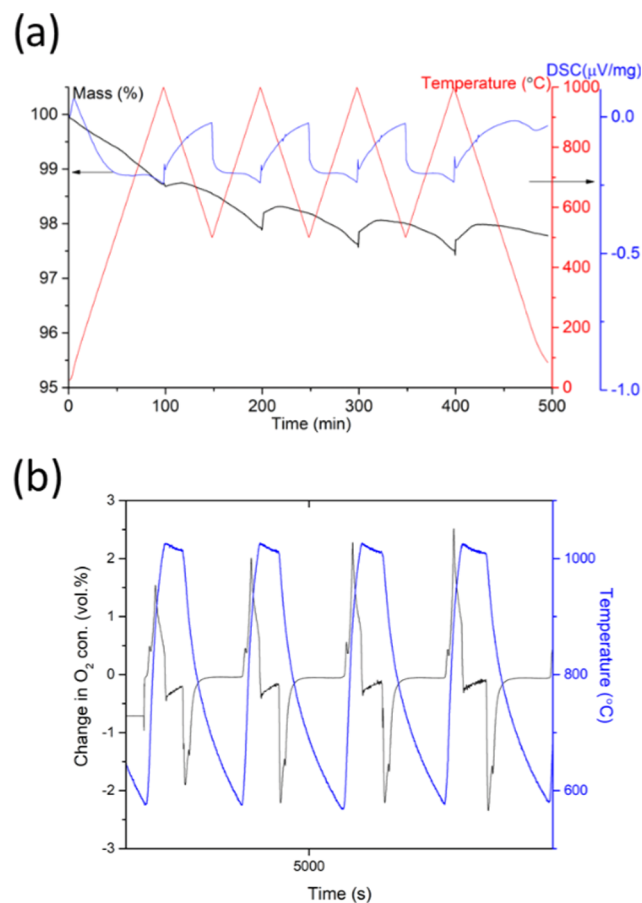
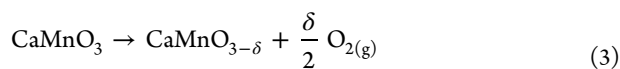
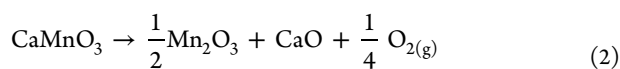
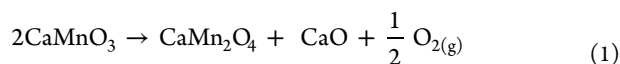


Figure 1. Thermal behavior of CM under controlled atmosphere (a) obtained by STA and O_2 release/consumption ability of CM in the fluidized bed test (b).

Table 2. Redox Properties of the Samples

sample	thermal analysis				fluidized bed experiments					
	$T_{\text{peak,ox}} (^{\circ}\text{C})$	$T_{\text{peak,red}} (^{\circ}\text{C})$	$\Delta w_{\text{ox}} (\%)$ (+)	$\Delta w_{\text{red}} (\%)$ (-)	$T_{\text{peak,ox}} (^{\circ}\text{C})$	$T_{\text{peak,red}} (^{\circ}\text{C})$	$\Delta VO_{2,\text{peak ox}} (\% \text{ av.})$ (+%)	$\Delta VO_{2,\text{peak red}} (\% \text{ av.})$ (-%)	$\Delta mO_{2,\text{ox}} (\text{+g, av.})$	$\Delta mO_{2,\text{red}} (\text{-g, av.})$
CM	795	970	0.2	0.4	885	970	2.20	2.22	0.23	0.31
CMF1	580	970	1.21	1.06	840	980	2.06	1.78	0.28	0.34
CMF2	610	975	1.06	1.02	830	980	1.69	1.64	0.24	0.32
CMM1	750	975	1.35	1.38	895	985	2.62	2.66	0.33	0.39
CMM2	770	980	1.32	1.37	885	980	2.08	2.05	0.29	0.37
CMC1	730	975	0.75	1.15	870	945	2.11	2.33	0.29	0.35
CMC2	740	970	0.9	1.20	860	950	2.66	2.74	0.34	0.41
CMCF	710	980	0.8	0.75	850	975	1.64	1.54	0.29	0.34
CMMT	770	980	0.5	1.05	830	980	1.05	1.31	0.15	0.21

behavior of CM in the fluidized bed test, respectively. The completion of a cycle involving heating and cooling takes 6000 s in STA, while it takes 1650 s in the fluidized bed test. These different time spans of applied thermocycles may affect the reaction kinetics, and different temperatures may be observed for redox cycles (Table 2). Possible reactions are given below (reactions 1–3). The expected mass loss for both reactions 1 and 2 is calculated as 5.6 wt % on average. The mass loss for reaction 3 may vary. Thermal analysis results showed that there was a mass loss of around 1.4 wt % within the first heating step, and the mass loss reached 2 wt % when the first cycle was completed. After the first cycle, the mass loss was around 0.4 wt % on average for each of the following cycles, while the mass gain was around 0.2 wt %. The reduction onset ($T_{\text{red,on}}$), where the reduction starts, and the peak temperature ($T_{\text{red,peak}}$), where the reduction was observed as maximum, were recorded as 700 and 970 °C, respectively. The oxidation onset temperature and the oxidation peak temperature were observed as 975 and 795 °C, respectively. It was reported that δ for $\text{CaMnO}_{3-\delta}$ is lower than 0.01 below 750 °C when the pO_2 is above 0.01 in the system.³⁶ In thermal analysis, pO_2 was set to 0.21 atm. From this point of view, most likely, only reactions 1 and 2 partly occurred simultaneously during the cycles in STA.



In the fluidized bed test, the result was slightly different. There was no significant temperature difference for reduction peaks between thermal analysis and fluidized bed test; however, the oxidation peak temperature observed in the fluidized bed test was around 90 °C higher than the thermal analysis. Since the heating and cooling rates in the fluidized bed are higher than those in the thermal analysis, different kinetic behavior may be expected for thermal analysis and fluidized bed test.^{37,38} The peak point of O_2 release/consumption during the cycles was obtained from the gas analyzer data (Figure 1b). The total O_2 release and consumption during the cycles were obtained via calculating the area under the oxidation and reduction peaks (Figure 1b). Two different phase transitions during both oxidation and reduction were reckoned to occur as there was a protrusion observed on the peaks. Theoretical O_2 release and consumption during redox reaction via reaction 1 are

calculated to be around 5.3 and 100 g of CaMnO_3 , respectively. Even though these values vary depending on δ for reaction 3, probably their averages will be lower than 1.12 and 100 g of CaMnO_3 , respectively.^{36,36} Reactions 1 and 3 may be pathways for the redox reactions in the fluidized bed test, as average O_2 consumption and release were detected around 0.23 and 0.31 g during oxidation and reduction, respectively. Most likely, the point where the protrusions were observed represents reaction 3, while the other peak was representative for where reaction 1 occurs. These formations were also revealed by XRD phase analysis after the fluidized bed tests (Figure S1), where $\text{CaMnO}_{3-\delta}$ along with a low amount of CaMn_2O_4 were observed. Even though CaMnO_3 has shown very promising performance for thermochemical energy storage applications in other studies,^{17,19,20,39} it did not show the best performance among the samples that were used in our study. This was already expected since the sample was already used as an oxygen carrier in a chemical looping oxygen uncoupling application, which may end up with decreased reactivity. The partial O_2 pressure in this study was 0.21 bar, which is close to the real applications, where air is used without dilution. It is known that the amount of released oxygen would increase when the pO_2 in the system decreases.¹⁸ As the other studies suggested that CaMnO_3 may be reduced via reaction 3, where pO_2 is lower than 0.18 atm,^{17,39} our study revealed that reaction 1 can also occur, where pO_2 is above 0.21 atm.

Promising results were obtained for both CLOU and TCES applications with Fe doping for CaMnO_3 .^{18,30,39} It has been revealed that Fe doping enhances the reversible redox reactions of CaMnO_3 and allows operation at higher temperatures than pure CaMnO_3 .³⁹ In this study, we used two different $\text{CaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1$ and 0.2), which have been used previously as an oxygen carrier in a CLOU application. The starting-phase compositions of $\text{CaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ and $\text{CaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ can be seen in Figures S2 and S3 in the Supporting Information, respectively. After the CLOU experiments, some CaMn_2O_4 formation was observed along with perovskite in both samples. In thermal analysis, the peak oxidation temperature was recorded as 580 °C, which is 215 °C lower than pure CaMnO_3 (Figure 2). A similar result was also observed in a related study, where the oxygen release onset temperature was lowered below 400 °C by Fe doping to CaMnO_3 .^{39,39} Like $\text{CaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$, $\text{CaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ also performed (Figure 3) a lower peak oxidation temperature (610 °C) than pure CaMnO_3 (795 °C). The reduction peak temperature was observed as 970 and 975 °C for $\text{CaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ and $\text{CaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$, respectively. However, almost 6 times higher mass gain was observed for

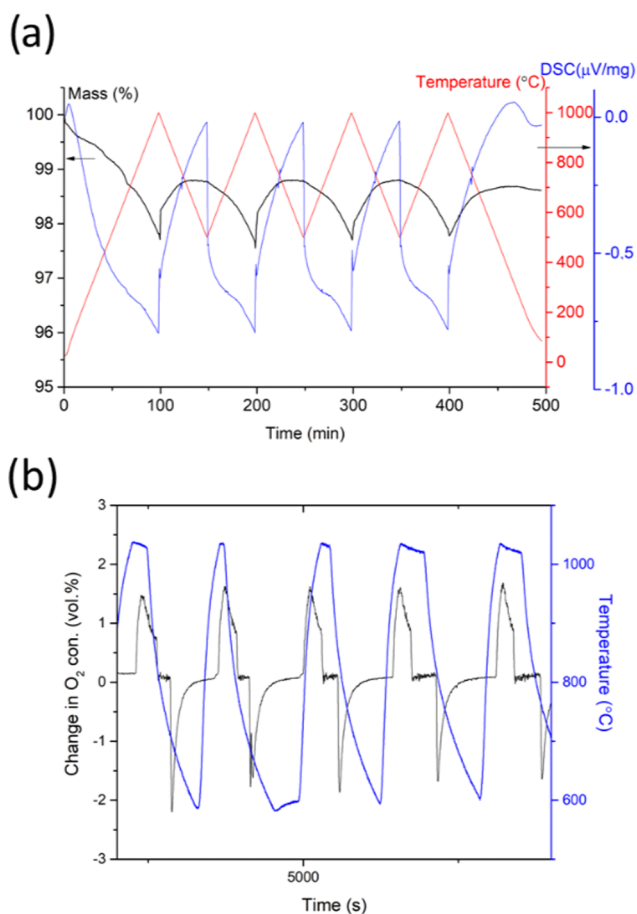


Figure 2. Thermal behavior of CMF1 under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMF1 in the fluidized bed test (b).

CaMn_{0.9}Fe_{0.1}O₃ and the mass loss was 2.65-fold higher than CaMnO₃ during oxidation and reduction, respectively. The mass gain/loss was recorded as 1.06 wt % during oxidation and 1.02 wt % during reduction.

Fe-doped CaMnO₃ samples showed higher redox peak temperatures in fluidized bed experiments than in thermal analysis. This result was not surprising considering the slow reduction kinetics of Fe oxides. In addition, pO₂ was set to 0.21 bar in the fluidized bed, which makes the reduction more difficult compared to lower pO₂ values since Fe oxides do not have oxygen release ability under these conditions. The oxidation peak temperature was recorded as 840 and 830 °C for CaMn_{0.9}Fe_{0.1}O₃ and CaMn_{0.8}Fe_{0.2}O₃, respectively, while the reduction peak temperature was 980 °C for both. In fluidized bed tests, CaMn_{0.9}Fe_{0.1}O₃ showed better performance than CaMn_{0.8}Fe_{0.2}O₃ with regard to the amount of O₂ released/consumed. Therefore, Fe-doped calcium manganese oxides can be easily put forward to enhance the redox properties of CaMnO₃ systems.

It is known that B-site dopant will have a higher impact than the A-site dopant on vacancy creation, which is related to the oxygen release ability of the compound.³⁶ However, the effect of MgO addition to the B site was tested for a CLOU application.^{32,40} A study revealed that MgO-doped CaMnO₃ showed good stability in a 50-cycle test and a small increase in reactivity was also observed.³² Both in thermal analysis and fluidized bed experiments (Figures 4 and 5 for CMM1 and

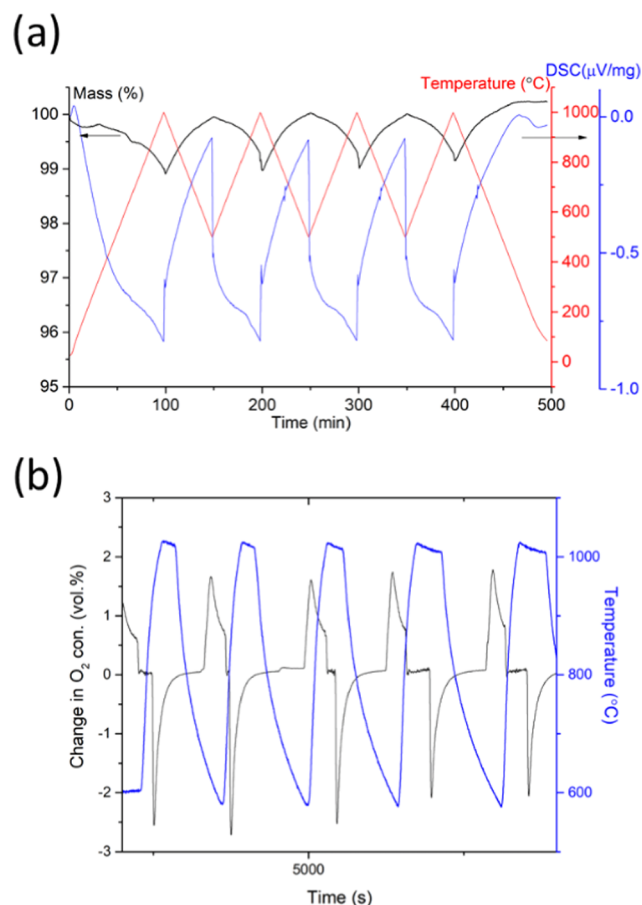


Figure 3. Thermal behavior of CMF2 under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMF2 in the fluidized bed test (b).

CMM2, respectively), the reduction peak temperature was observed around 975–985 °C for both MgO-doped CaMnO₃. However, the oxidation peak temperature was obtained as 750 °C in thermal analysis, while it was 895 °C in fluidized bed test for CaMn_{0.9}Mg_{0.1}O₃. This difference most likely occurred due to the slow reoxidation kinetics of the CaMnO₃, like the other doped CaMnO₃ samples. This temperature difference between the experiments was also observed for CaMn_{0.8}Mg_{0.2}O₃, as expected. The phase analysis of the fresh and used samples of CMM1 and CMM2 revealed that there was free MgO in the system along with the perovskite structure (Figures S4 and S5). Most likely, a part of the perovskite dissociated into MgO and Ca₂MnO₄ during a previous CLOU application. There was no free MgO in the starting sample before it had been used in a CLOU application. However, as the intensity ratio of the MgO was different in the fresh sample (after CLOU) than in the used sample (after fluidized bed tests), MgO dissociation was thought to have occurred during the experiments. Even though there was only a 25–45 °C temperature difference for the oxidation peak temperature of MgO-doped CaMnO₃ samples and pure CaMnO₃ in the thermal analysis, the mass gain was 6.75 times higher for CaMn_{0.9}Mg_{0.1}O₃ and 5 times higher for CaMn_{0.8}Mg_{0.2}O₃ than for pure CaMnO₃. A similar result was obtained in the fluidized bed tests as well. The average oxygen peak release was recorded as 2.66 vol % for CaMn_{0.9}Mg_{0.1}O₃ for reduction steps. The peak oxygen consumption was recorded around 2.62 vol % for oxidation steps. Among the MgO-doped samples, the best results were obtained with

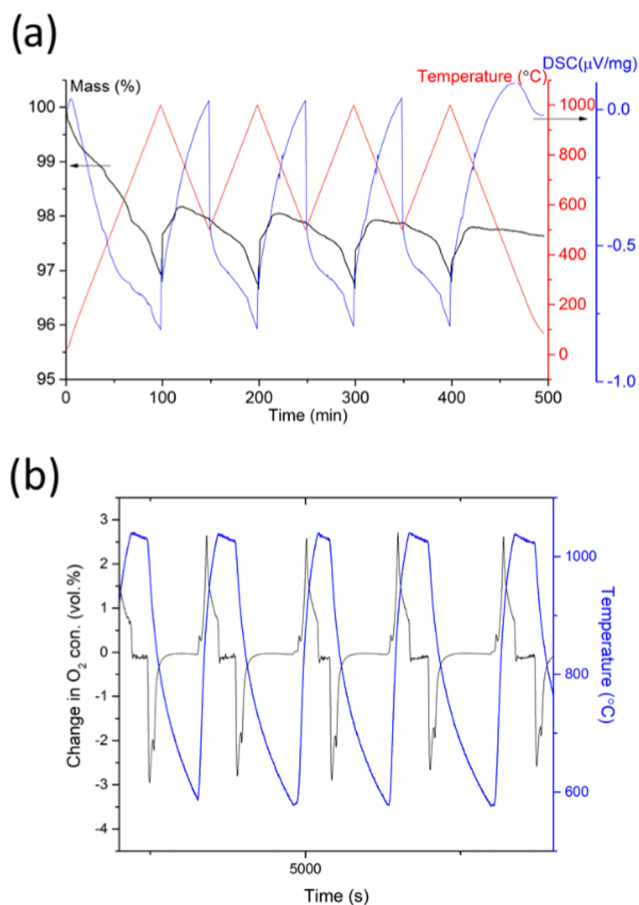


Figure 4. Thermal behavior of CMM1 under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMM1 in the fluidized bed test (b).

CaMn_{0.9}Mg_{0.1}O₃. The different redox characteristics of the MgO-doped CaMnO₃ samples and the pure CaMnO₃ supported that MgO was still present in the perovskite system despite the observed phase dissociation.

Cu is one of the most well-known materials both for both chemical looping oxygen uncoupling and thermochemical energy storage applications.^{14,41,42} However, a support material to combine with CuO is generally proposed due to the low melting point and the relatively high cost of the pure copper compounds.⁴³ From this point of view, CuO-doped CaMnO₃ samples were also tested in this study. The phase analyses of CMC1 and CMC2 are presented in Figures S6 and S7, respectively. In Figure 6, the simultaneous thermal analysis and fluidized bed test results were given for CaMn_{0.9}Cu_{0.1}O₃. The reduction peak temperature was obtained as 975 and 945 °C in the thermal analysis and the fluidized bed test, respectively. There was only a 25 °C difference observed between pure CaMnO₃ and CaMn_{0.9}Cu_{0.1}O₃ for the reduction peak temperature in the fluidized bed test. This difference most likely occurred due to the CuO addition. This hypothesis was also supported by the results of CaMn_{0.2}Cu_{0.2}O₃ (Figure 7). The difference for the reduction peak temperature was obtained to be around 20 °C between pure CaMnO₃ and CaMn_{0.8}Cu_{0.2}O₃. The oxidation peak temperatures were observed to 730 and 740 °C, while it was found to be 795 °C for pure CaMnO₃. The difference for the recorded oxidation peak temperature was smaller in the fluidized bed tests between CuO-doped CaMnO₃ (870 and 860 °C, respectively) and pure CaMnO₃.

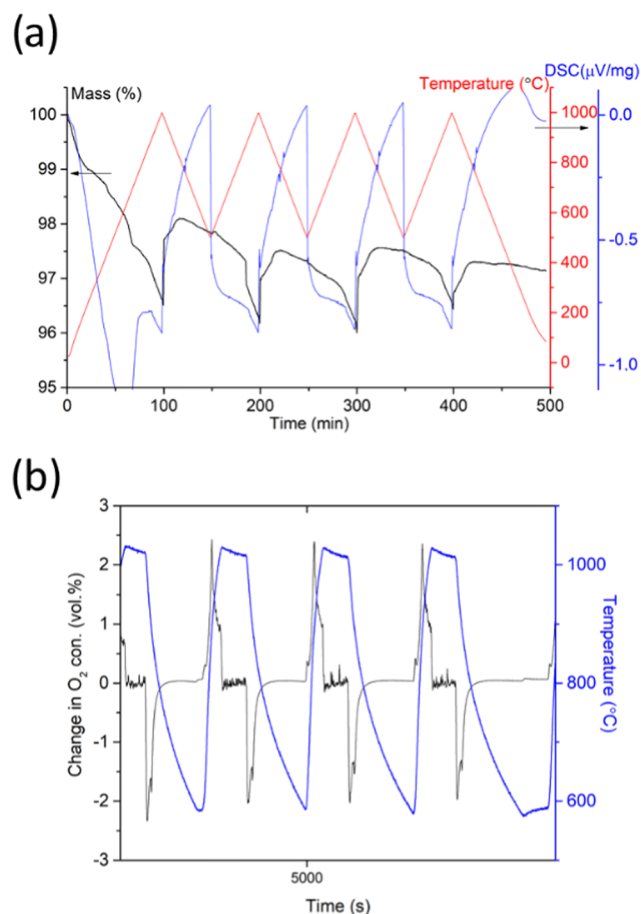


Figure 5. Thermal behavior of CMM2 under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMM2 in the fluidized bed test (b).

Copper affected the mass gain/mass loss positively in the thermal analysis. During the oxidation cycles, 0.75 wt % mass gain was observed for CaMn_{0.9}Cu_{0.1}O₃. For CaMn_{0.2}Cu_{0.2}O₃, it was even higher and recorded as 0.9 wt %. During the reduction cycles, the mass loss was obtained as 1.15 and 1.2 wt % for CaMn_{0.9}Cu_{0.1}O₃ and CaMn_{0.2}Cu_{0.2}O₃, respectively. Fluidized bed tests also showed a similar result to thermal analysis. During the oxidation cycles, average O₂ consumption by CaMn_{0.9}Cu_{0.1}O₃ and CaMn_{0.2}Cu_{0.2}O₃ was 0.29 and 0.34 g, respectively. During the reduction cycles, 0.35 g of O₂ was released by CaMn_{0.9}Cu_{0.1}O₃ and the value was 0.41 g for CaMn_{0.2}Cu_{0.2}O₃. Among the tested samples, Cu-doped CaMnO₃ showed one of the best performances together with Mg-doped CaMnO₃.

The combined transitional-metal doping to CaMnO₃ has also been studied.^{29,30} As both Fe and Cu dopings show better performance than pure CaMnO₃, the effect of the combined doping of Cu and Fe was tested as well (Figure 8). In addition, a well-studied oxygen carrier CMMT^{26,32,33} was also tested after being used in a CLOU application. Despite the individual high performance of Cu- and Fe-doped CaMnO₃ samples, Cu- and Fe-doped CaMnO₃ could not show the same performance in the thermal analysis tests. This most likely occurred due to the phase dissociation after the CLOU operation (Figure S8). However, as the dissociated compounds may also exhibit redox behavior, the performance of the material was still promising. The peak reduction temperature obtained from the thermal

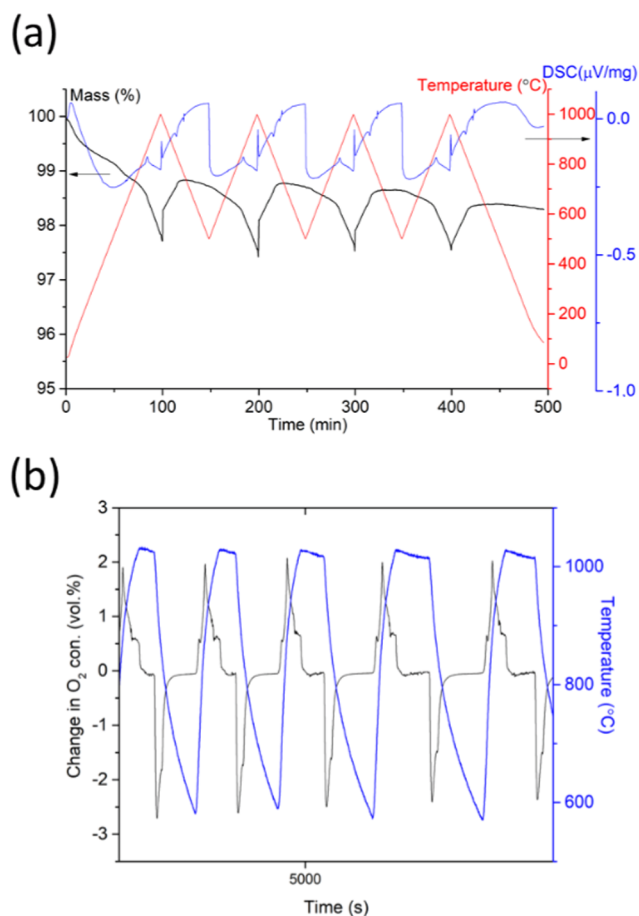


Figure 6. Thermal behavior of CMC1 under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMC1 in the fluidized bed test (b).

analysis was similar (980 °C) to CMF and CMC (970–975 °C). However, the oxidation peak temperature of CMCF was recorded as 710 °C, which was similar to that of the CMC samples (730–740 °C) but quite higher than that of the CMF samples (580–610 °C). The mass gain during oxidation and the mass loss during the reduction were recorded as 0.8 and 0.75 wt %, respectively. Even though CMCF did not exhibit the best performance, it was more stable than other samples in a manner of cyclic mass change. For the fluidized bed tests, there was no significant temperature difference observed between the CMCF, CMF, and CMC. However, CMCF also showed a way better performance than pure CM sample. CMC, CMF, and CMCF consumed and released similar amounts of O₂ during the redox cycles in the fluidized bed tests. However, CMCF exhibited slower kinetics, which can be explained by the wider and shorter O₂ consumption/releasing peaks than CMC and CMF samples.

CMMT was mentioned in the literature as a stable and high-performance oxygen carrier for CLOU.^{26,32,33} However, CMMT could not show a high TES performance in this study. There was no significant temperature difference between CMMT, CMM, and CM for the redox peak temperatures when comparing the thermal analysis and the fluidized bed tests (Figure 9). The mass loss/gain performance of CMMT was almost 40% lower than that of CMM samples in the thermal analysis. However, CMMT showed 2.5 times higher mass gain/loss than CM. The fluidized bed test performance of

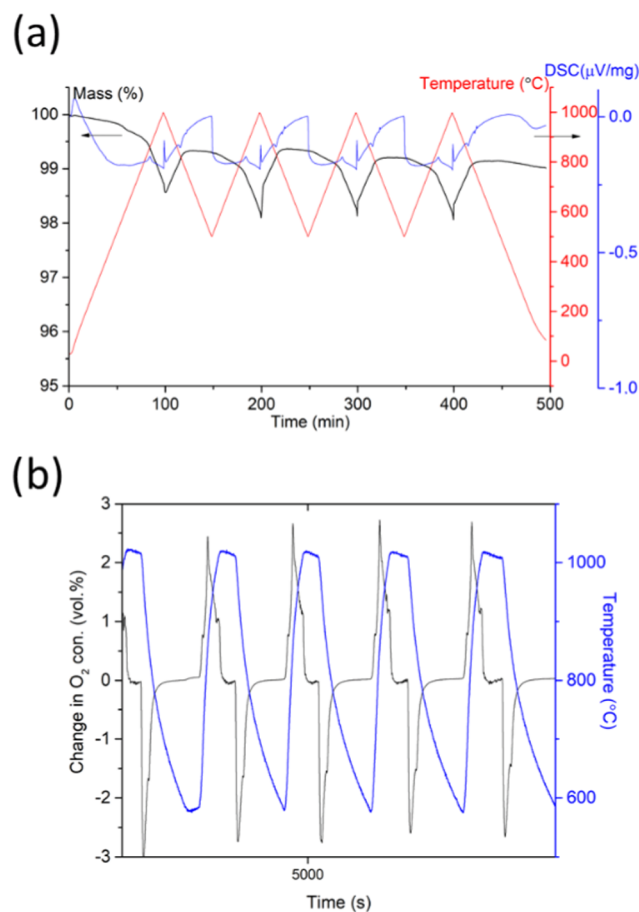


Figure 7. Thermal behavior of CMC2 under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMC2 in the fluidized bed test (b).

CMMT was slightly different from that of the thermal analysis. In the fluidized bed tests, CMMT exhibited even lower O₂ uptake/release performance than CM. The decrease in the performance most likely occurred due to a new phase formation, Ti_{0.9}Mg_{0.1}O₅, which was detected via phase analysis (Figure S9).

DISCUSSION

Thermochemical energy storage (TCES) applications are crucial to store energy in a clean way and to conserve the primary energy sources.⁴⁴ Therefore, it offers an opportunity to help reduce greenhouse gas emissions.⁴⁴ Carbon capture and storage (CCS) technologies are also important to tackle climate change.⁴⁵ Recently, materials can be used in both thermochemical energy storage applications and carbon capture and storage applications.⁴⁶ For both applications, the candidate materials should be cost-effective, environmentally friendly, and thermochemically stable.^{47,48} Since a high amount of materials are needed in industrial applications for both methods, it would be valuable to recycle the “used” materials by another application or to use a low-cost material such as waste or ore. From this point of view, promising doped CaMnO₃-based oxygen carriers used in chemical looping oxygen uncoupling (CLOU) applications were tested for potential TCES. Calcium manganite-based samples were designed to have a certain composition, which is given in Table 1 when they were synthesized for CLOU applica-

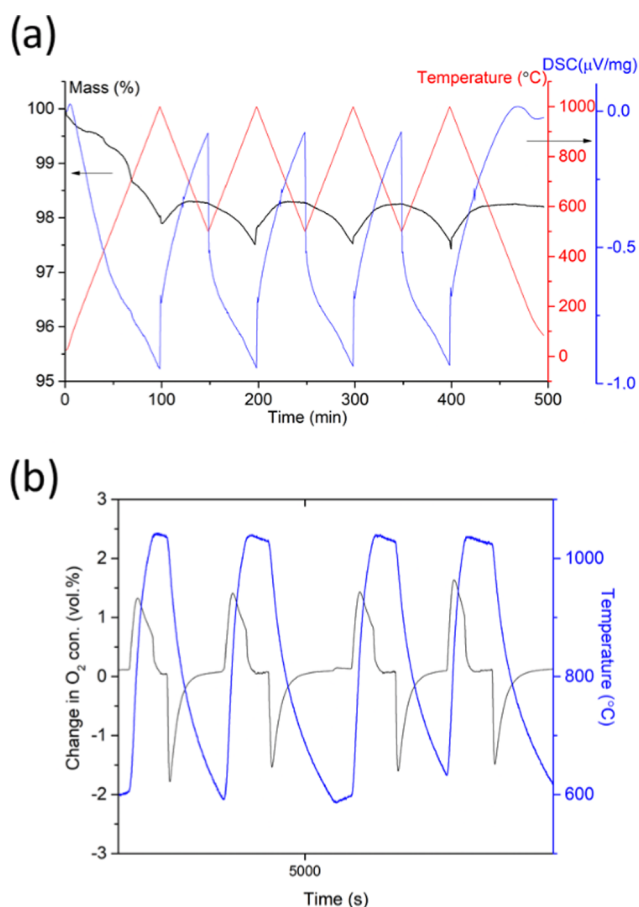


Figure 8. Thermal behavior of CMCF under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMCF in the fluidized bed test (b).

tions.^{26,29–33} A fresh material that is not used in any CLOU operation would most likely exhibit a higher performance than that obtained in this study, since perovskite-based materials are well known as good candidates for thermochemical energy storage applications.⁴⁹ Even though fresh materials were beyond the scope of this study, phase analysis was carried out on both fresh samples and used samples in a CLOU application to reveal the effect of the CLOU operation on the phase structure of the samples. However, no difference was observed regarding phase structure, which was also observed in other related studies.^{29,31} Although the metal oxide-based CLOU and TCES applications are similar in the oxidation manner, CLOU has a harsher reduction step, where a fuel is used as the reduction tool. Therefore, we have tested the used material in a CLOU application to mimic the worst-case scenario in a manner of thermochemical stability.

Fluidized bed experiments were used to investigate the oxygen release/consumption behavior of the samples related to temperature changes, whereas thermal analysis combined with differential scanning calorimetry could reveal the possible phase transitions without weight loss/gain in the system. It is important to use a sufficiently large amount of sample in the tests to mimic the real applications. However, the amount of sample used is very limited in the thermal analysis experiments for practical reasons. But thermal analysis results are important to reveal thermodynamic characteristics and to mimic the ideal conditions, where the heating and cooling rates are predefined and strictly controlled. From this point of view, simultaneous

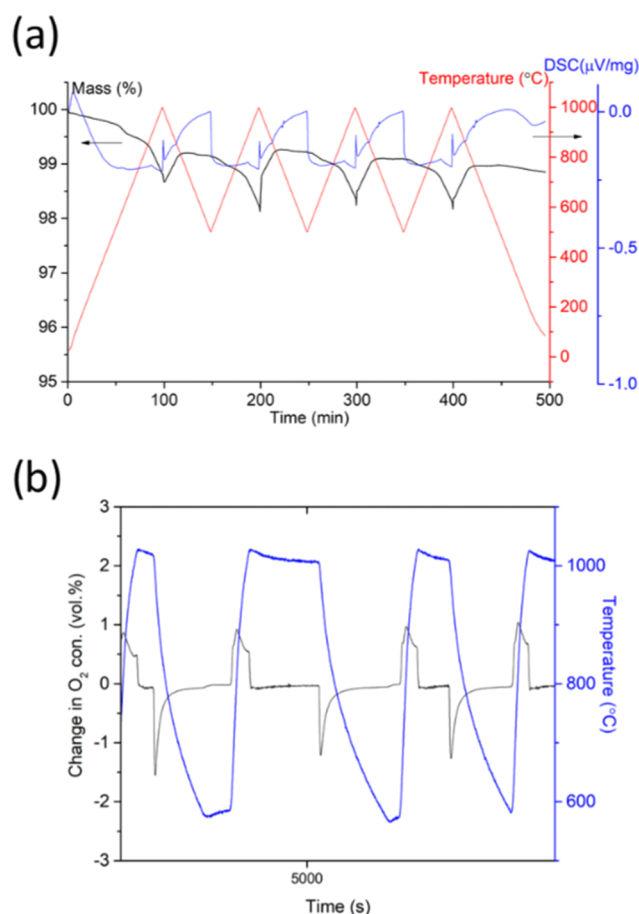


Figure 9. Thermal behavior of CMMT under controlled atmosphere (a) obtained by STA and O₂ release/consumption ability of CMMT in the fluidized bed test (b).

thermal analysis and fluidized bed tests were used as complementary techniques in this study.

Decomposition of the particles into a smaller size can be observed in a reduction step, and an oxidation step may cause some agglomeration due to the sintering effect in CLOU applications.⁵⁰ Therefore, before testing the particles in fluidized bed experiments or in thermal analysis, the samples were sieved into the 180–250 μm size range to ensure that all particles have the same size range without any fragmented particles. After the fluidized bed experiments, all samples were investigated under a scanning electron microscope and secondary electron images were recorded to investigate the thermomechanical and morphological stabilities of the particles (Figure S10). It is worth noting that the number of redox cycles applied should be increased to have better understanding of the thermomechanical stability of the oxygen carriers. However, the poorest thermomechanical stability after the applied cycles was observed on Fe-doped CaMnO₃ samples, while the Cu- and Fe-doped CaMnO₃ samples showed the highest thermomechanical stability.

Among the samples, the highest O₂ release/consumption in the fluidized bed tests was obtained with the CaMn_{0.8}Cu_{0.2}O₃ sample. For thermal analysis experiment, CaMn_{0.9}Mg_{0.1}O₃ showed the best performance for the highest mass change. From DSC curves, the heat storage capacities were calculated for the samples that showed the best performance. The heat storage capacity was calculated as 280 kJ/kg for

CaMn_{0.9}Mg_{0.1}O₃ and 430 kJ/kg for CaMn_{0.8}Cu_{0.2}O₃. The heat storage capacity of pure CaMnO₃ was also calculated (240 kJ/kg) to reveal the difference of CM, CMM1, and CMC2. The obtained heat storage capacity of pure CM was slightly lower than the reported values in the literature.³⁹ Most likely, this difference occurred due to the formation of CaMn₂O₄ in the pure CM sample after the CLOU operation.

CONCLUSIONS

In this work, calcium manganite-based oxides used in chemical looping oxygen uncoupling (CLOU) applications were tested as a potential thermochemical energy storage material. The dopant effects of Fe₂O₃, MgO, CuO, Fe₂O₃&CuO, and MgO&TiO₂ were also investigated to compare their performance with pure CaMnO₃. Even though materials may end up with decreased reactivity after being used in CLOU applications, the results showed that promising calcium manganites for CLOU applications showed good performance also for thermochemical energy storage applications. The highest O₂ release/reoxidation performance among the tested samples was exhibited by CaMn_{0.8}Cu_{0.2}O₃, and the heat storage capacity was calculated as 430 kJ/kg CaMn_{0.8}Cu_{0.2}O₃. However, CaMn_{0.9}Mg_{0.1}O₃ showed the best cyclic stability, which is also important for materials' lifetime. This study showed that the utilization of recycled CLOU materials in a thermochemical energy storage application may be possible if a chosen oxygen carrier shows high cyclic stability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c05182>.

Detailed characterization of the samples (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was funded by Adlerbertska Foundation (21285157) and Iris Stipendiet (IR2020-0195).

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