

Highly Efficient Oxygen-Storage Material with Intrinsic Coke Resistance for Chemical Looping Combustion-Based CO₂ Capture

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Chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) are emerging thermochemical CO₂ capture cycles that allow the capture of CO₂ with a small energy penalty. Here, the development of suitable oxygen carrier materials is a key aspect to transfer these promising concepts to practical installations. CuO is an attractive material for CLC and CLOU because of its high oxygen-storage capacity (20 wt%), fast reaction kinetics, and high equilibrium partial pressure of oxygen at typical operating temperatures (850–1000 °C). However, despite its promising characteristics, its low Tammann temperature requires the development of new strategies to phase-stabilize CuO-based oxygen carriers. In this work, we report a strategy based on stabilization by co-precipitated ceria (CeO_{2-x}), which allowed us to increase the oxygen capacity, coke resistance, and redox stability of CuO-based

Introduction

According to the Intergovernmental Panel on Climate Change (IPCC), global warming and climate change are most likely because of the increasing concentration of CO_2 in the atmosphere.^[1] In this context, the implementation of CO_2 capture and storage (CCS) technologies is considered as a mid-term solution to stabilize or even reduce the concentration of CO_2 in the atmosphere.^[2,3] Among the different CCS technologies, chemical looping combustion (CLC), conceptually linked to oxy-fuel combustion, is arguably the most promising approach with regards to economics and environmental impact.^[4] In CLC, a hydrocarbon is oxidized by lattice oxygen provided by a so-called oxygen carrier (typically a transition metal oxide) according to Equation (1):

$$(2n+m)Me_{x}O_{y}(s)+C_{n}H_{2m} \to (2n+m)Me_{x}O_{y-1}(s)+nCO_{2}(g)+mH_{2}O(g)$$
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oxygen carriers substantially. The performance of the new oxygen carriers was evaluated in detail and compared to the current state-of-the-art materials, that is, AI_2O_3 -stabilized CuO with similar CuO loadings. We also demonstrate that the higher intrinsic oxygen uptake, release, and mobility in CeO_{2-x} -stabilized CuO leads to a three times higher carbon deposition resistance compared to that of AI_2O_3 -stabilized CuO. Moreover, we report a high cyclic stability without phase intermixing for CeO_{2-x} -supported CuO. This was accompanied by a lower reduction temperature compared to state-of-the-art AI_2O_3 -supported CuO. As a result of its high resistance towards carbon deposition and fast oxygen uncoupling kinetics, CeO_{2-x} -stabilized CuO is identified as a very promising material for CLC-and CLOU-based CO_2 capture architectures.

After the condensation of steam, a pure stream of CO_2 is produced. To close the cycle, the reduced oxygen carrier is re-oxidized with air [Eq. (2)]:

$$2\operatorname{Me}_{x}O_{y-1}(s)+O_{2}(g) \rightarrow 2\operatorname{Me}_{x}O_{y}(s) \tag{2}$$

A schematic diagram of the CLC process is shown in Figure 1. A modification of the CLC concept is chemical looping with oxygen uncoupling (CLOU). In CLOU, a hydrocarbon reacts with molecular oxygen [Eq. (3)] that is released by a redox reaction of the oxygen carrier [Eq. (4)]:

$$2\operatorname{Me}_{x}O_{y}(s) \to \operatorname{Me}_{x}O_{y-1}(s) + O_{2}(g) \tag{4}$$

The advantage of CLOU over CLC is its faster rate of combustion, and it is, therefore, particularly attractive for solid fuels. CLC for solid fuels, for example, coal or biomass, first requires a slow gasification step to convert the solid fuel into a synthesis gas, whereas the solid fuel can react directly with the molecular oxygen released by the oxygen carrier in CLOU. However, CLOU puts additional thermodynamic constraints on the oxygen carrier such as a sufficiently high oxygen partial pressure at typical operating temperatures, which thus further limits the number of suitable transition metal oxides.

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Figure 1. Schematic diagram of CLC.

Oxygen carriers used commonly for CLC include the oxides of Ni, Mn, Fe, and Cu. In addition, a number of naturally occurring materials, for example, illmenite and manganese ores, have also received some attention.^[5] However, as a result of the additional thermodynamic constraints, CLOU materials have been limited essentially to CuO-, Mn₂O₃-, and perovskitebased oxygen carriers. $^{\ensuremath{\scriptscriptstyle [6]}}$ CuO is particularly attractive for CLC because of its (i) high oxygen carrying capacity (0.2 $g_{0,}g_{Cu0}^{-1}$), (ii) high reactivity with hydrocarbons, (iii) exothermic reduction reactions, and (iv) low tendency for carbon deposition. In addition, CuO is a suitable candidate for CLOU as it is able to release oxygen at the typical operating temperatures of 850-1000 °C. However, the quantity of oxygen released is reduced to $0.1 g_{0,} g_{CuO}^{-1}$ under CLOU conditions because of its intrinsically limited stoichiometric oxygen change (to Cu₂O) in the temperature range of 850–1000 °C. In this paper, the reduction of CuO to Cu₂O in an inert atmosphere is referred to as decomposition. Nonetheless, the main challenge associated with the use of CuO for CLC and CLOU is its structural instability with successive redox cycles as its low Tammann temperature overlaps with the operating temperature of the CLC and CLOU processes. The Tammann temperature, defined empirically as $0.5T_{\rm m}$ ($T_{\rm m}$ in K), indicates the onset of sintering. The Tammann temperatures of CuO, Cu_2O, and Cu are 526, 481, and 405 $^\circ\text{C}\textsc{,}$ respectively. Thus, irreversible microstructural changes are to be expected for CuO-based oxygen carriers during CLC and CLOU operation as the cationic diffusion of the material is activated at high operating temperatures and sintering and agglomeration will proceed continuously. A strategy to phase-stabilize the material is the use of so-called cermets that are composed of a metallic and a ceramic phase. Examples of cermets are mixtures of CuO/Cu and a ceramic support such as Al₂O₃, MgAl₂O₄, sepiolite (Mg₂Si₆O₁₅(OH)₂·6H₂O), SiO₂, TiO₂, MgO, or ZrO₂.^[7] The ceramic support structure may be also used to manipulate the redox characteristics of the material and the activity of its surface and may, indeed, even contribute to the overall oxygen carrying/uncoupling capacity of the material. Importantly, a large number of the cermets tested so far have revealed unfavorable reactions between the metal oxide and the ceramic phases which, in turn, often result in compounds that show significantly reduced redox kinetics and oxygen release such as CuAl₂O₄^[8,9] and Cu₂MgO₃.^[10] As a result of its low tendency to intermix with metallic phases, we believe that ceriabased cermets have a high potential for chemical looping. Furthermore, ceria-based cermets can contribute to the storage and release of oxygen by a nonstoichiometric redox reaction. The binary oxide ceria, CeO_{2-xr} is a mixed ionic-electronic conducting material for which the Ce^{4+}/Ce^{3+} oxidation states are balanced by its oxygen nonstoichiometry.^[11,12] Ceria has a simple cubic structure,^[13] possesses a high Tammann temperature (1064 °C),^[14,15] and shows no intermixing in the CuO- CeO_{2-x} system.^[16,17]

Very recently, Hedayati et al.^[18] reported promising CO₂ capture capacities for ceria and gadolinia-doped ceria-copper oxide cermets. Defect thermodynamics, given in Brouwer diagrams, show that doping (such as gadolinia-doped (10 mol%) ceria) shifts the electrolytic domain boundary of the oxide by orders of magnitude towards higher oxygen partial pressures^[11,19] (for typical CLC and CLOU operation temperatures). This has serious consequences for chemical looping applications as the uptake and release of oxygen from Gd-doped CeO_{2-x} is strongly decreased for oxygen partial pressures that are typically encountered during the reduction step in chemical looping. Hence, in this work we only study copper-ceria cermets with pristine ceria supports as a new class of materials for CLC and CLOU.

In this work we replace the current state-of-the-art cermet for CLC and CLOU (i.e., Al₂O₃-stabilized CuO) with CeO_{2-x}-supported CuO. To this end, we develop and determine unequivocally the potential of undoped, CeO_{2-x} -supported CuO cermets for CLC and CLOU. The cyclic redox stability (using CH₄ as a fuel) and oxygen release capacity are investigated in detail and discussed in light of the microstructure and the phase characteristics of the cermets. The materials were synthesized using a co-precipitation technique, and we focus on cermets that contain up to 60 wt % CuO. The performance of the new CeO_{2-x}-based cermets is compared to state-of-the-art Al₂O₃-stabilized CuO. We are able to demonstrate that a rational choice of the support can substantially increase the resistance of the oxygen carrier towards unfavorable carbon deposition and increase both the oxygen capacity and release rates for CLC and CLOU-based CO₂ capture applications.

Results and Discussion

Characterization of freshly calcined oxygen carriers

The chemical phases of the calcined oxygen carriers were determined using XRD. The XRD patterns of CeO_{2-x} -stabilized CuO (50 and 60 wt%) and the reference material, Al_2O_3 -stabilized CuO (50 wt%), are plotted in Figure 2. In the oxidized state, the CuO-CeO_{2-x} oxygen carriers are composed of the targeted monoclinic and cubic fluorite structure of CuO and CeO_{2-xr} respectively. The diffractograms show only peaks for ceria^[11,20] and copper(II) oxide.^[21] The presence of additional intermixed phases between CuO (or Cu) and CeO_{2-x} was not observed, which confirms the high chemical stability of these materials. For comparison, the diffractogram of the state-of-theart Al_2O_3 -stabilized CuO-based oxygen carrier (50 wt% CuO) is

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Figure 2. X-ray diffractograms of the freshly calcined oxygen carriers: a) Cu50Ce, b) Cu60Ce, and c) Cu50Al. The following compounds were identified: (\bullet) Cu0, (\bullet) CeO_{2-x}, and (\blacksquare) CuAl₂O₄.

plotted in Figure 2 c. XRD reveals the formation of spinel $CuAl_2O_4$ (cubic structure)^[22] in addition to the presence of CuO. Notably, the formation of intermixed phases may affect the redox kinetics of the material, however, this will be assessed in more detail later. Peaks characteristic of Al_2O_3 were not observed in the freshly calcined material.

The average crystallite sizes of CuO, CeO_{2-xr} and $CuAl_2O_4$ in the oxygen carriers are given in Table 1 along with the values for the surface area, pore volume, and crushing strength of the materials. It can be seen that the crystallite size of CuO is very similar in all the oxygen carriers synthesized. N₂ adsorption measurements confirm that the high calcination temperature

Table 1. Surface area, pore volume, crushing strength, and average crystallite sizes of CuO, CeO_{2-xr} and $CuAl_2O_4$ in the synthesized oxygen carriers.							
Property	Cu50Ce	Material Cu60Ce	Cu50Al				
surface area $[m^2g^{-1}]$ pore volume $[cm^3g^{-1}]$ crushing strength [N] CuO ₍₂₀₀₎ [nm] CeO _{2-x'(111)} [nm] CuAl ₂ O _{4'(311)} [nm]	12.9±1.6 30 52 -	< 0.5 < 0.05 10.9 ± 1.9 32 59 -	12.3±2.8 33 - 49				

of 1000 °C resulted in cermets with a low surface area and pore volume. Previous studies indicated that a low surface area and pore volume do not have a detrimental effect on the redox characteristics of CuO-based oxygen carriers.^[23] Finally, the crushing strength of all of the oxygen carriers was in the range of 10.9–12.9 N. The obtained crushing strengths are sufficiently high to allow the CLC and CLOU performance of the materials to be assessed in a fluidized bed. This high mechanical strength of the material synthesized is of significant relevance for practical applications.

SEM was used to analyze the surface morphology of the calcined oxygen carriers. Figure 3a and b show that the surface of Cu50Ce and Cu60Ce was composed of tightly packed polyhedrons. For Cu60Ce, small grains decorated the surface of the larger polyhedrons. Energy-dispersive X-ray (EDX) analysis of Cu50Ce showed that CuO and CeO_{2-x} were distributed uniformly in the cermet (Figure 4). For Cu60Ce, the large polyhedrons comprised only CuO, whereas the comparatively smooth grains contained only CeO_{2-x} (Figure 4). For comparison, the surface morphologies of pure, that is, unsupported, CuO and CeO_{2-x} were also studied. High-resolution scanning electron micrographs of CuO and CeO_{2-x} are shown in Figure S1. Pure CuO possessed a very smooth and nonporous surface, whereas the surface of pure CeO_{2-x} comprised nano-sized grains with an average size of 96 ± 24 nm. For the CuO-Al₂O₃ cermets, the surface of Cu50Al was fairly smooth and composed (partly) of very small grains (Figure 3 c). The average size of the grains was 142 ± 24 nm. EDX mapping of the surface revealed that the small grains are composed mainly of CuO, whereas the smooth structures contained both CuO and Al₂O₃ (Figure S2). The nonhomogeneous distribution of CuAl₂O₄ in Cu50Al may limit the suitability of this material for CLC and **CLOU** applications.

Temperature-programmed decomposition and reduction

To investigate the oxygen release (uncoupling) characteristics of the freshly calcined oxygen carriers, temperature-programmed decomposition (TPD) experiments were performed. For comparison, the TPD characteristics of unsupported CuO and CeO_{2-x} were also determined. Plots of the normalized weight change as a function of temperature are shown in Figure 5. The onset of the decomposition reaction was defined as the temperature at which the oxygen carrier had lost 2% of



Figure 3. Scanning electron micrographs of the oxygen carriers calcined at 1000 °C: a) Cu50Ce, b) Cu60Ce, and c) Cu50Al.





Figure 4. EDX maps of freshly calcined a) Cu50Ce and b) Cu60Ce.



Figure 5. TPD profiles of the synthesized oxygen carriers: (---) CuO, (---) Cu50Ce, (----) Cu60Ce, (----) Cu50Al, and (---) CeO_{2-x}.

the total weight loss. Similarly, the decomposition reaction was considered complete once 98% of the total weight loss had been reached. The decomposition of CuO (4CuO (s) \rightarrow 2Cu₂O (s)+O₂ (g)) in N₂ started at \sim 737 °C and was completed at ~946 °C. However, CeO_{2-x} did not decompose in the temperature range studied here. For the synthesized oxygen carriers, the decomposition of CeO_{2-x}-stabilized CuO started at a slightly higher temperature (~775 $^\circ\text{C})$ but was completed at an appreciably lower temperature of ~895 $^\circ\text{C}$ compared to that of unsupported CuO. A decrease of the loading of CuO in CuO- CeO_{2-x} cermets led to a further decrease of the decomposition temperature: a very favorable behavior for CLOU applications. Notably, detailed XRD analysis of the decomposed materials confirmed that the CuO-CeO_{2-x} oxygen carriers possessed a stable cermet structure that did not show any intermixing in the temperature range studied here (Figure S3). In contrast, the decomposition of phase-intermixed Cu50Al started at a substantially higher temperature (~827 °C) compared to that of CeO_{2-x}-stabilized CuO and pure CuO. The decomposition of Cu50Al was only completed when the holding period at 1000 °C was reached. The shift of the decomposition temperature of Cu50Al to higher temperatures can be explained by the

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presence of $CuAl_2O_4$ that decomposes according to Equation (5):

$$\begin{array}{l} 4\,{\rm CuAl_2O_4}~(s)\to 4\,{\rm CuAlO_2}~(s) \\ +2\,{\rm Al_2O_3}~(s){\rm +O_2}~(g) \end{array} \tag{5}$$

XRD analysis of decomposed Cu50Al (Figure S3) confirmed the presence of CuAlO₂ and Al₂O₃. Thus, CeO_{2-x}-stabilized CuObased oxygen carriers are superior to Al₂O₃-stabilized CuO because of their high chemical stability (i.e., no phase intermixing) and, in turn, reduced decomposition temperature. The CuO content of the synthesized oxygen carriers, determined

from the weight loss during decomposition, is given in Table 2. For all oxygen carriers, the CuO content determined by TPD is close to the theoretically expected values.

Table 2. CuO content of the oxygen carriers as determined from TPD.							
Property	Cu50Ce	Material Cu60Ce	Cu50Al				
CuO content [wt%]	52	60	51				

CH₄ temperature-programmed reduction (TPR) and Raman spectroscopy of CeO_{2-x}⁻ and Al₂O₃-supported CuO, pure CuO, and pure CeO_{2-x} were performed to determine their reduction characteristics and pathways and the extent of carbon deposition. The CH₄-TPR profiles of the oxygen carriers (Figure 6) show that the reduction of unsupported CuO occurred in the temperature range 535–895 °C by an apparently single-step reaction [Eq. (6)]:

$$4 \operatorname{CuO} (s) + \operatorname{CH}_4 (g) \to 4 \operatorname{Cu} (s) + \operatorname{CO}_2 (g) + 2 \operatorname{H}_2 O (g)$$
(6)



Figure 6. CH₄-TPR profiles of the synthesized oxygen carriers: (----) CuO, (----) Cu50Ce, (-----) Cu50CAI, and (----) CeO_{2-x}.

ChemSusChem 2015, 8, 2055 – 2065



Once CuO was fully reduced to metallic Cu, no further increase in sample weight (because of carbon deposition) was observed. Nonetheless, the Raman spectrum of the reduced material showed minor peaks at $\tilde{\nu} = 1360$ and 1582 cm^{-1} , which are characteristic for graphite (Figure S4). Raman spectroscopy is expected to have a higher sensitivity to carbon deposition than thermogravimetry. The peak at $\tilde{\nu} = 1360 \text{ cm}^{-1}$ originates from defects in the graphite structure, whereas the peak located at $\tilde{\nu} = 1582 \text{ cm}^{-1}$ corresponds to the deformation of carbon bonds in the basal planes of the hexagonal structure of graphite. Thus, the Raman measurements indicate that unsupported Cu has a small tendency for carbon deposition by the reaction shown in Equation (7):

$$\mathsf{CH}_4 \ (g) \to \mathsf{C} \ (s) + 2 \,\mathsf{H}_2 \ (g) \tag{7}$$

The TPR experiments also showed that the slow reduction of CeO_{2-x} to Ce_2O_3 (using CH₄) started at ~765 °C but was not completed within the measurement time (even for a holding time of 30 min at 1000 $^{\circ}$ C). Both Ce₂O₃ and CeO_{2-x} were identified in the X-ray diffractogram of the reduced material (Figure S5). Furthermore, no carbon is deposited on pure CeO_{2-x} (Figure S4). For CeO_{2-x}-stabilized CuO, reduction started at ~490°C, that is, at a lower temperature compared to pure CuO, and progressed by a two-step mechanism. The first reduction step occurred in the temperature range 490-735°C, which is followed by a second reduction step in the temperature range 850-985°C. Once the reduction of Cu50Ce and Cu60Ce was complete, a slow increase in sample weight was observed, indicative of carbon deposition by the reaction shown in Equation (7). To elucidate the reduction mechanism of CeO_{2-x}-stabilized CuO, the TPR experiment was stopped at the temperatures marked in Figure 6. Subsequently, the partially reduced oxygen carriers were analyzed by XRD and Raman spectroscopy. The X-ray diffractograms of Cu50Ce revealed that in the first reduction step only CuO was reduced to Cu (Figure 7 a). In the second reduction step CeO_{2-x} is partially reduced to Ce₂O₃. The Raman spectra allowed us to elucidate further the prevailing near-order cationic-anionic lattice changes during reduction (Figure 7b). As a result of its cubic symmetry, CeO_{2-x} shows a single, characteristic Raman F_{2a} stretching mode for the cationic-oxygen anionic vibrations (peak at around $\tilde{\nu} =$ 463.3 cm⁻¹ for 700 °C). This is in agreement with values reported previously.^[13, 14, 24, 25] A more detailed analysis of the changes of the bulk cationic-anionic bond strength of the CeO_{2-x} constituent in the oxygen carrier as a function of the reduction temperature was performed by assessing the shift in the F_{2q} peak position carefully (insets in Figure 7b and Figure S6). We observed a significant blueshift and decrease of the F_{2g} stretching mode wavenumber (by -1.8 cm^{-1}) with increasing reduction temperature (+300 °C). This near-order chemomechanical change of CeO_{2-x} is in agreement with previous reports.^[26] The blueshift in the CeO_{2-x}-based cermet structure is indicative of an expansion of the bulk CeO_{2-x} lattice as a result of the reaction of the lattice oxygen of CeO_{2-x} with carbon (or carbon precursors).^[27,28] Consequently, carbon deposition was not observed after the completion of the first reduc-

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Figure 7. a) X-ray diffractograms of (partially) reduced Cu50Ce. The following compounds were identified: (\bullet) Cu, (\bullet) CeO_{2-x} and (\blacktriangle) Ce₂O₃. b) Raman spectra of (partially) reduced Cu50Ce: (\longrightarrow) $T = 735 \,^{\circ}$ C, (---) $T = 850 \,^{\circ}$ C, and (•••••) $T = 1000 \,^{\circ}$ C, 30 min.

tion step, which confirms the high potential of ceria-based cermets for CLC and CLOU. Furthermore, the Raman measurements allowed us to conclude that CeO_{2-x} is also reduced during the first reduction step.

In the CH₄-TPR profile of Cu50Al, we observe a first weight loss in the temperature range 550-810°C. This is followed by an increase in weight in the temperature range 810-860 °C and a second weight loss in the temperature range 860- $970\,^\circ\text{C}.$ Towards the end of the TPR experiment, an increase in sample weight was observed. To better understand the TPR profile of Cu50Al, XRD and Raman spectroscopy were performed at the temperatures marked in Figure 6. At both 810 and 860 °C, Cu and CuAl₂O₄ were identified in the X-ray diffractograms (Figure 8a) of partially reduced Cu50Al. The intensity of the CuAl₂O₄ peaks decreased with increasing temperature. However, Raman spectroscopy confirmed that graphite was already present on the surface of partially reduced Cu50Al (810 and 860°C; Figure 8 b). The Raman spectrum shows an increase in the intensity of the graphite peaks with increasing temperature (Figure 8b). This confirms that Cu50Al has a high tendency for carbon formation. If we combine the XRD, Raman spectroscopy, and TPR results for Cu50AI we can conclude that the rate of carbon deposition was higher than the rate of re-



Figure 8. a) X-ray diffractograms of (partially) reduced Cu50AI. The following compounds were identified: (\bullet) Cu, (\blacksquare) CuAl₂O₄, and (\square) Al₂O₃. b) Raman spectra of (partially) reduced Cu50AI: (\longrightarrow) T=810 °C, (---) T=850 °C, (•••••) T=970 °C, and (-•-•) T=1000 °C, 30 min.

duction in the temperature range 810–860 °C. Intriguingly, between 860 and 970 °C, only a slight increase in the intensity of the graphite peaks (Figure 8b) was observed, which indicates that the quantity of carbon deposited did not change significantly in this temperature range. The decrease in weight in the temperature range 860–970 °C is, therefore, caused by the very slow reduction of CuAl₂O₄. This reduction step was completed at ~970 °C. The X-ray diffractogram of Cu50Al sampled at 970 or 1000 °C (after a holding time of 30 min) showed only peaks for Cu and Al₂O₃. Finally, the increase in weight from 970 °C until the end of the TPR experiment was because of additional carbon deposition, as confirmed by Raman spectroscopy.

CLC and CLOU performance

The cyclic oxygen release (uncoupling) capacity and the partial pressure of the oxygen released were determined for the different materials in a fluidized bed at 950 °C. Plots of the quantity of O_2 released by the decomposition of 1 g of oxygen carrier as a function of cycle number are shown in Figure 9. For Cu50Ce and Cu60Ce, the amount of O_2 released during the first cycle was lower than the theoretically expected value because Cu50Ce and Cu60Ce were not fully decomposed during the first cycle (a fixed decomposition time of 120 s was used).



Figure 9. Quantity of oxygen released by the different oxygen carriers determined in a fluidized bed at 950 °C: (\odot) Cu50Ce, (\bigtriangleup) Cu60Ce, and (\blacksquare) Cu50Al. The duration of the decomposition and reoxidation reactions was fixed to 120 and 180 s, respectively. The dashed and dotted horizontal lines indicate the theoretical oxygen uncoupling capacity of oxygen carriers that contain, respectively, 50 and 60 wt % CuO.

This is confirmed by the composition profile of the sampled off-gas (Figure S7). Nonetheless, the rate of O2 release increased with cycle number to result in a gradual increase in the amount of O₂ released over the first six cycles. From the sixth cycle, the rate of O₂ release was sufficiently high to achieve the full decomposition of the oxygen carriers within 120 s to yield an oxygen release very close to the theoretically expected value (Figure 9). To elucidate the reason for the increasing decomposition rate with cycle number, the BET surface area of the cycled oxygen carriers was measured and found to be $< 0.5 \text{ m}^2\text{g}^{-1}$. Therefore, changes in the surface area cannot be responsible for the increase in the rate of O₂ release with cycle number. However, scanning electron micrographs of the cycled oxygen carriers revealed changes in their surface morphology (Figure S8). The surface of the cycled oxygen carriers is composed of CuO and CeO_{2-x} grains with steps and edges. Moreover, the crystallite size of CuO and CeO_{2-x} increased during cycling (Table S1). Thus, the increasing rate of the decomposition reaction with cycle number may be attributed to structural changes in the material that facilitate the release and transport of O_2 .

Cu50Al possessed a stable but very low oxygen uncoupling capacity of only 0.18 mmol_{O2} $g_{carrier}^{-1}$, that is, ~88% lower than the theoretically expected value of 1.6 mmol_{O2} $g_{carrier}^{-1}$. The low oxygen uncoupling capacity of Cu50Al is because of the slow decomposition of CuAl₂O₄ as observed previously in the TPD experiments.

The partial pressure of O_2 released by Cu50Al and Cu50Ce during the 10th CLOU cycle is plotted in Figure 10. The decomposition of Cu50Ce started once the oxygen concentration in the fluidized bed reached ~6 mol m⁻³. This somewhat higher than theoretically expected oxygen partial pressure (at 950 °C) can be explained by the fact that the previous exothermic oxidation step caused an increase in the bed temperature by ~15 °C. The continuous decrease in the O_2 concentration shown in Figure 10 is because only 1 g of oxygen carrier was used in the fluidized bed experiments. Nonetheless, the data shown in Figure 10 demonstrate that CeO_{2-x}-stabilized CuO



Figure 10. Concentration profile of O₂ released during the 10th decomposition step for a) Cu50Ce and b) Cu50Al. The experiment was performed at 950 °C in a fluidized bed. The dotted line (-----) plots the oxygen concentration during a blank experiment, whereas the horizontal dashed lines (----) correspond to the equilibrium oxygen concentration at 950 and 965 °C.

can provide an O_2 atmosphere very close to the theoretically expected equilibrium concentration. For Cu50Al, the O_2 concentration decreased in a very similar manner to the blank experiment (fluidized bed without any oxygen carrier) because of the slow rate of O_2 release of CuAl₂O₄.

The cyclic redox characteristics of the synthesized oxygen carriers were assessed in a fluidized bed at 900 $^\circ\text{C}$ using methane for reduction (10 vol% CH₄ and 90 vol% N₂). The composition of the off-gas during the 10th redox cycle is plotted in Figure 11 a and b for Cu50Ce and Cu50Al, respectively. From the plot shown in Figure 11a it can be seen that when the atmosphere was switched from air to N₂, the mole fraction of O₂ stabilized at ~0.012 because of the spontaneous decomposition of CuO to Cu₂O. The partial pressure of O₂ is close to the thermodynamically predicted equilibrium partial pressure of oxygen at 900 °C of 0.014. After we switched from N₂ to a CH₄ atmosphere, a sharp increase in the mole fraction of CH₄ occurred. An induction period for the reduction of partially decomposed Cu50Ce with CH₄ can be seen clearly (Figure 11 a, inset). After the induction period, the mole fraction of CH₄ decreased because of the reaction of CH₄ with CeO_{2-x}-stabilized

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Figure 11. Off-gas composition for the 10th redox cycle performed at 900 °C for a) Cu50Ce and b) Cu50AI: (----) CH₄, (•••••) CO₂, (---) CO, and (----) O₂. A mixture of 10 vol% CH₄ in N₂ was used to reduce the oxygen carrier. The reduction time was fixed to 180 s.

CuO to produce CO₂, H₂O, and metallic Cu. The formation of CO is caused by the partial oxidation of CH₄ by CeO_{2-x}. The isothermal reduction of Ce50Ce, as observed in the fluidized bed, is in agreement with the CH₄-TPR results. A small CO₂ peak at the start of the oxidation step is indicative of carbon deposition by the reaction shown in Equation (7), albeit to a very small extent. The deposition of carbon on the cermet is most likely to occur during the partial oxidation of CH₄.

For Cu50Al, the concentration of O_2 was found to decrease continuously when the inlet gas was switched from air to N_2 (Figure 11 b). This behavior can be explained by the slow release of oxygen by CuAl₂O₄, as noted previously (Figure 10). After switching to a CH₄ atmosphere, the mole fraction of CO₂ increased rapidly. Cu50Al reacts instantaneously with CH₄, that is, an induction period as seen for CeO_{2-x}-stabilized CuO was not observed (Figure 11 b, inset). Again, the CO₂ peak is followed by a CO peak that is most likely caused by the partial oxidation of CH₄ by "oxygen-depleted" Cu50Al.^[8] Compared to Cu50Ce, a large peak of CO₂ was observed during the reoxidation of Cu50Al in air, which indicates that a high quantity of carbon is deposited on Cu50Al. If we assume the complete oxidation of CH₄ to CO₂, the normalized yield of CO₂ is defined as [Eq. (8)]:

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Normalized yield of
$$CO_2 = \frac{MOI_{CO_2 measured}}{MOI_{CO_2 produced theoretically}}$$
 (8)

The normalized yield of CO₂ is plotted for each oxygen carrier studied as a function of cycle number in Figure 12. The normalized yield of CO₂ for Cu50Ce is stable and ~0.85 over the 25 redox cycles tested. Normalized yields less than 1 can be explained by the fact that the oxygen carrier was partially de-



Figure 12. Normalized yield of CO₂ as a function of cycle number determined from the CLC experiments performed in a fluidized bed at 900 °C: (●) Cu50Ce, (▲) Cu60Ce, and (■) Cu50Al. The duration of the reduction reaction was fixed to 180 s.

composed during the N₂ purge segment, as shown in Figure 11 a. For Cu60Ce, the average normalized yield of CO₂ remained close to 0.95 over the 25 cycles tested. However, this oxygen carrier showed agglomeration over the 25 redox cycles test. Agglomeration of the oxygen carrier is a serious concern as it can lead to defluidization. A possible explanation for the agglomeration tendency of Cu60Ce is the phase separation of CuO and CeO_{2-x} during calcination (Figure 4b). No agglomeration was observed for the material with the lowest Cu loading (Cu50Ce). This observation confirms that the structure of the oxygen carrier is directly related to its performance. Notably, the three redox cycles performed by Hedayati et al.^[18] are insufficient to assess the agglomeration characteristics of CeO_{2-x}supported CuO-based oxygen carriers that contain 60 wt% CuO. Thus, the maximal loading of CuO that allowed a stable operation was ~ 50 wt %. However, for Cu50Al the average normalized yield of CO2 remained stable at ~0.85 during the 25 redox cycles tested. The low yield of CO₂ for Cu50Al can be explained by the partial oxidation of CH₄ during the end of the reduction step (Figure 11 b).

Plots of the quantity of carbon deposited during CH₄ reduction are shown in Figure 13. Cu50Ce showed a comparatively low tendency for carbon deposition, whereas the quantity of carbon deposited on Cu60Ce increased with cycle number. The consistently low quantity of carbon deposited on Cu50Ce can be explained by the ability of surface oxygen of CeO_{2-x} to react with carbonaceous species according to Equation (9):^[29,30]





Figure 13. Amount of carbon [mol] deposited by CH₄ decomposition during CLC operation in a fluidized bed at 900 °C as a function of cycle number: (●) Cu50Ce, (■) Cu50Al, and (▲) Cu60Ce. The duration of the reduction reaction was fixed to 180 s.

However, the quantity of carbon deposited on Cu60Ce increased with cycle number. A possible explanation might be that the inhomogeneous intermixing of CuO and CeO_{2-x} phases in Cu60Ce results in agglomeration, which thereby reduces the availability of surface oxygen required for the removal of carbonaceous species. For Cu50Al, an approximately three times higher quantity of carbon was deposited compared Cu50Ce. As discussed above, for Cu50Al the decomposition of CH₄ starts during CuO reduction. Thus, a high (and somewhat fluctuating) quantity of carbon is expected.

The high CO selectivity of CeO_{2-x}-supported CuO-based oxygen carriers during reduction would reduce the efficiency of the CLC process. In addition, carbon deposition would result in the release of CO₂ in the air reactor, which thus limits the overall CO₂ capture efficiency of the process. It can be seen for Cu50Ce that the formation of CO and the deposition of carbon can be avoided by a judicious choice of the reduction time (Figure 11 a). If the duration of the reduction segment was reduced from 180 to 30 s, CO and carbon deposits were not observed (Figure 14). Plots of the amount of CO₂ produced if the reduction time was set to 30 s are shown in Figure 15. Initially, the amount of CO₂ produced increased over the first 10 cycles but subsequently stabilized at an average value of 1.43 mmol CO₂. Notably, the average amount of CO₂ produced is very close to the theoretically expected value of 1.57 mmol CO_2 under CLOU conditions. Furthermore, the evolution of CO₂ with cycle number is similar to the trend observed for the release of O₂ (Figure 9). This indicates that CH₄ was primarily oxidized by the molecular oxygen released. The increasing rate of reduction with cycle number is most likely linked to changes in the morphology and the crystallite size of CuO in the oxygen carrier (Table S1 and Figure S9).

Conclusions

We demonstrated that CeO_{2-x}-stabilized CuO-based oxygen carriers possess a high and stable oxygen release under chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) conditions. At the same time the

 $n \operatorname{C+CeO}_{2-x} \rightarrow \operatorname{CeO}_{2-x-n} + n \operatorname{CO}$

(9)



Figure 14. Composition of the off-gases during the 10th redox cycle at 900 °C for Cu50Ce: (——) CH₄, (•••••) CO₂, (—) CO, and (–––) O₂. A mixture of 10 vol% CH₄ in N₂ was used to reduce the oxygen carrier. The reduction time was fixed to 30 s.



Figure 15. Amount of CO₂ [mol] produced as a function of cycle number (Cu50Ce at 900 $^\circ$ C). The reduction time was fixed to 30 s.

cermet structure is maintained. We confirmed that conventional Al₂O₃-stabilized CuO-based structures show an intermixing of phases that results in the formation of CuAl₂O₄, which has unfavorable material characteristics for the CLC and CLOU processes. Furthermore, the new class of material benefits from its intrinsic nonstoichiometric oxygen changes and its capability to effectively remove carbon precursors, which thus minimizes carbon deposition. XRD analysis confirmed that no unfavorable intermixed phases were formed for CuO-CeO_{2-x} cermets. Temperature-programmed decomposition and CH₄ temperatureprogrammed reduction experiments revealed that the rate of O₂ release and reduction was higher for CeO_{2-x}-stabilized CuO than unsupported CuO and Al₂O₃-stabilized CuO. CeO_{2-x}-stabilized CuO was reduced by a two-step mechanism. In the first step, CuO and CeO_{2-x} were reduced simultaneously, whereas in the second step only CeO_{2-x} was partially reduced to CeO_{2-x}/Ce_2O_3 . Importantly, carbon deposition did not occur during CuO reduction with CH₄. Raman-based near-order bulk analysis of the anionic-cationic bonding of ceria revealed clearly that the oxygen nonstoichiometry increased and that lattice oxygen (released by CeO_{2-x}) contributes to the increased resistance to carbon formation of these cermets. In contrast, state-of-the-art, Al₂O₃-stabilized CuO was reduced in a single step and significant carbon deposition was observed, which indicates an enhanced CH_4 decomposition activity for this material.

Cyclic CLOU experiments performed in a fluidized bed at 950°C revealed that CeO_{2-x}-stabilized CuO released oxygen very close to the theoretically expected equilibrium oxygen partial pressure. The cyclic O₂ release of CeO_{2-x}-stabilized CuO was initially low but increased with cycle number to reach the theoretically expected value after five cycles. However, Al₂O₃stabilized CuO showed a very low cyclic O2 release because of the slow rate of CuAl₂O₄ decomposition. Under CLC conditions, all of the oxygen carriers synthesized showed stable CO2 yields. However, CeO_{2-x}-stabilized CuO that contained 60 wt% CuO was found to agglomerate most likely because of phase separation between CuO and CeO_{2-x}. Importantly, CeO_{2-x}-stabilized CuO showed an approximately three times lower quantity of carbon deposited compared to Al₂O₃-stabilized CuO. With the use of Raman spectroscopy, we confirmed that the oxidation of deposited carbon occurred by the lattice oxygen of CeO_{2-x}. As a result of their high and stable O₂ release, high equilibrium partial pressure of O2, and high resistance to carbon deposition and agglomeration, CeO_{2-x}-stabilized CuObased cermets that contain 50 wt% CuO were identified as highly promising materials for CLC- and CLOU-based CO₂ capture architectures.

Experimental Section

Oxygen carrier synthesis

CeO_{2-x}-supported CuO-based oxygen carriers that contain 50 or 60 wt% CuO were prepared using a co-precipitation technique. Typically, appropriate amounts of $Cu(NO_3)_2 \cdot 2.5 H_2O$ and Ce(NO₃)₃·6H₂O were dissolved in reverse-osmosis water (100 mL, 15 M Ω cm at 25 °C). Subsequently, a 2 M NaOH solution was fed dropwise into the nitrate solution under magnetic stirring until a pH value of 10.0 was reached. The resulting precipitate was aged for 150 min at RT and subsequently washed several times with reverse-osmosis water to remove excess Na⁺ and nitrate ions. Once the electrical conductivity of the filtrate was $\sim 150 \ \mu S \ cm^{-1}$, the cake of washed precipitate was dried at 100 °C for 24 h. The dried material was calcined in a muffle furnace at 1000°C for 2 h using a heating rate of 5 °C min⁻¹. Finally, the calcined oxygen carrier was crushed and sieved into the size ranges 53–106 and 300–425 $\mu m.$ For comparison, an Al₂O₃-supported CuO-based oxygen carrier that contained 50 wt% CuO was synthesized using a similar protocol (co-precipitation was performed at pH 8.5, and $AI(NO_3)_3 \cdot 9 H_2O$ was used as the Al precursor). The following nomenclature is used to describe the oxygen carriers: the symbol Cu is followed by the weight percentage of CuO and an abbreviation of the support (i.e., Ce or Al). For example, Cu60Ce is a CeO_{2-x}-stabilized cermet/ oxygen carrier that contains 60 wt % CuO.

Oxygen carrier characterization

The composition of the calcined, reduced, and cycled oxygen carriers was determined by XRD (Bruker D8 Advance). The diffractometer was mounted with a Lynx eye super speed detector and operated at 40 kV and 40 mA using CuK_a radiation. The X-ray diffractograms were acquired within the range of $2\theta = 20-80^{\circ}$ with a step



size of 0.0275° per second. The average crystallite sizes of CuO, $CeO_{2-x\prime}$ and $CuAl_2O_4$ in the oxygen carriers were estimated using Scherrer's equation. $^{[31]}$

 N_2 physisorption isotherms of the calcined and cycled oxygen carriers were acquired at -196 °C by using a Quantachrome NOVA 4000e analyzer. Before the acquisition of the isotherms, the oxygen carriers were degassed at 300 °C for at least 2 h. The BET^[32] and Barrett–Joyner–Halenda (BJH)^[33] models were used to calculate the surface area and pore volume from the N_2 isotherms, respectively.

The crushing strength of the oxygen carriers was obtained by measuring the force required to break the oxygen carrier particles by using a Shimpo force gauge. Here, 20 measurements were averaged to determine the mean crushing strength of the oxygen carriers.

A Leo Gemini 1530 SEM was used to characterize the surface morphology of the freshly calcined and cycled oxygen carriers. Doublesided carbon tape was used to attach the oxygen carriers to an aluminum holder. The oxygen carriers were sputter-coated with Pt before imaging. EDX mapping was performed to analyze the surface composition of the synthesized materials.

TPD and TPR experiments were performed by using a thermogravimetric analyzer (TGA, Mettler Toledo TGA/DSC 1) to determine, respectively, the decomposition and reduction characteristics of the synthesized oxygen carriers. Typically, a small quantity (~20 mg) of the oxygen carrier (53–106 μ m) was heated from RT to 1000 °C at a rate of 10 °C min⁻¹ under a flow of N₂ or 10 vol% CH₄ in N₂ (25 mLmin⁻¹). Subsequently, the sample was kept at 1000 °C for 30 min. In all experiments, a constant N₂ flow of 25 mLmin⁻¹ was used as a purge flow over the microbalance. The reduced oxygen carriers were further characterized by Raman spectroscopy (Thermo Scientific DXR Raman microscope). The materials were excited with a 480 nm laser. For every material, three spectra were taken and averaged.

Cyclic redox and oxygen release performance

The cyclic CLC and CLOU performance of the synthesized oxygen carriers was evaluated by using a fluidized-bed reactor at 900 and 950 °C, respectively. A schematic diagram of the experimental setup is given in Figure S10. Typically, $\mathrm{Al}_2\mathrm{O}_3$ was fluidized by N_2 at a flow rate of 2 Lmin⁻¹ (25 °C, 1 bar) and heated either to 900 or 950 °C. Once the temperature in the fluidized bed stabilized, the oxygen carrier (1 g, 300-425 µm) was added to the fluidized bed and 25 CLC or CLOU cycles were performed. The flow rate of the inlet gas was set to 2 L min⁻¹ (25 °C, 1 bar) in each segment of a cycle. The duration of the oxygen release (decomposition), reduction, and reoxidation reactions were fixed to 120, 180, and 180 s, respectively. The reactor was purged for 30 s with N₂ after each reaction segment. The oxygen uncoupling reaction was performed in a N₂ atmosphere, whereas a mixture of 10 vol% CH₄ in N₂ was used for reduction. The oxygen carriers were oxidized using 10.5 vol% O₂ in N₂ and air for CLOU and CLC, respectively. The amount of O₂, CO₂, and CO produced during the CLOU and CLC reactions was calculated according to Equations (10)-(12):

$$N_{\rm O_2} = V_{\rm N_2} \times \int \frac{y_{\rm O_2}}{1 - y_{\rm O_2}} dt \tag{10}$$

$$N_{\rm CO_2} = V_{\rm CH_4/N_2} \times \int y_{\rm CO_2} dt \tag{11}$$

$$N_{\rm CO} = V_{\rm CH_4/N_2} \times \int y_{\rm CO} dt \tag{12}$$

In which $N_{O_2'}$, N_{CO_2} , and N_{CO} are, respectively, the number of moles of O_2 , CO_2 , and CO produced in each cycle, V_{N_2} and V_{CH_4/N_2} are the molar flow rates of N₂ and 10 vol % CH₄ in N₂, and $y_{O_2'}$, $y_{CO_2'}$, and y_{CO} are, respectively, the mole fractions of O_2 , CO_2 , and CO in the dried off-gases.

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