Structure-performance relationship of Cu-based oxygen carriers for thermo-chemical CO₂ capture cycles

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Structure-performance relationship of Cu-based oxygen carriers for thermo-chemical CO₂ capture cycles

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This work is dedicated to the memory of my grandmother (died 2013)
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Abstract

Global warming and climate change are most likely linked to the increasing concentration of CO$_2$ in the atmosphere. Therefore, it is imperative to develop and implement processes that avoid the emission of anthropogenic CO$_2$. One possible near- to mid-term solution is carbon dioxide capture and storage. In this context, the so-called chemical looping combustion (CLC) process is particularly attractive due to its very low CO$_2$ capture costs when compared to the currently available technology, i.e. amine scrubbing. In CLC, lattice oxygen from an oxygen carrier is used to combust a hydrocarbon yielding, after the condensation of steam, a pure stream of CO$_2$ suitable for sequestration. To allow the application of CLC to solid fuels, chemical looping with oxygen uncoupling (CLOU) has been proposed. Here molecular oxygen is provided via the reduction of the oxygen carrier in an inert atmosphere, thus, the solid fuel is combusted effectively in an oxyfuel-type mode. A cornerstone of the CLC and CLOU processes is the development of suitable oxygen carriers.

Among the transition metal oxides typically considered for CLC and CLOU, CuO stands out owing to its high oxygen carrying capacity, exothermic reduction reactions, fast reduction kinetics and high equilibrium partial pressure of O$_2$ at typical operating temperatures (850–1000 °C). However, the low Tammann (sintering) temperature of CuO is a serious drawback. In this context, it has been proposed to stabilize CuO on high Tammann temperature supports such as Al$_2$O$_3$ or MgAl$_2$O$_4$, thus, reducing the morphological changes occurring over repeated redox operation.

In this work, a co-precipitation technique was developed to synthesize CuO-based oxygen carriers. The redox characteristics of the oxygen carriers were interpreted in the light of the detailed morphological characterization of the synthesized materials and a synthesis-structure-performance relationship was developed. It was found that both the precipitating agent and the pH at which the precipitation was performed influenced strongly the structure and chemical composition of the oxygen carriers. Moreover, the influence of different synthesis parameters, such as CuO content and calcination temperature, on the redox stability of oxygen carriers synthesized was systematically accessed. The results showed that the mechanical and structural properties of the oxygen carriers can be adjusted via the calcination temperature.
In CuO-Al$_2$O$_3$ systems, avoiding the formation of the CuAl$_2$O$_4$ spinel is key to obtaining a material with a high redox stability. A Na$^+$ doping strategy was investigated to phase stabilize Al$_2$O$_3$-supported CuO, yielding in turn an inexpensive material with a high redox stability and CO$_2$ capture efficiency. Utilizing in-situ and ex-situ X-ray absorption spectroscopy, the local structure of Cu and the reduction pathways of CuO were determined as a function of the Na$^+$ content and cycle number.

To increase the coke resistance of CuO, ceria (CeO$_{2-x}$) stabilized, CuO-based materials were developed. The performance of the new oxygen carriers was evaluated in detail and compared to Al$_2$O$_3$-stabilized CuO with similar CuO loads. It was shown that the higher intrinsic oxygen mobility in CeO$_{2-x}$-stabilized CuO led to a three times higher carbon deposition resistance when compared to Al$_2$O$_3$-stabilized CuO.

It has been proposed that the redox performance of the oxygen carriers depends critically on the conduction pathways for the transport of ions and electrons. In this context, the influence of the formation of a percolation network on the rate of oxidation reaction was investigated using CuO as the active metal oxide and CeO$_{2-x}$ as the support. Conductivity and performance measurements showed that the activation energy for charge transport through the oxygen carrier increased with decreasing Cu content, lowering in turn the rates of oxidation.

Finally, MgAl$_2$O$_4$-stabilized, Cu-modified, Fe$_2$O$_3$-based redox materials were developed for thermochemical water splitting. The material possessed a high reactivity with CH$_4$ and low rates of carbon deposition. To elucidate the effect of Cu doping on reducing significantly the rate of carbon deposition (while not affecting negatively the high redox activity of the material) extended X-ray absorption fine structure spectroscopy and energy dispersive X-ray spectroscopy were employed.
Zusammenfassung


der CuO-Gehalt und die Kalzinierungstemperatur. Die Ergebnisse zeigen, dass die mechanischen und strukturellen Eigenschaften der Sauerstoffträger über die Kalzinierungstemperatur geregelt werden können.


Um die Kohlenstoffablagerung auf CuO zu reduzieren, wurden Ceria(CeO₂ₓ)-stabilisierte, CuO-basierte Materialien entwickelt. Die Aktivität der neuen Sauerstoffträger wurde ausführlich mit der Aktivität von Al₂O₃-stabilisiertem CuO mit ähnlichen CuO Gehalt verglichen. Es wurde gezeigt, dass die höhere intrinsische Sauerstoffmobilität im CeO₂ₓ-stabilisierten CuO zu einer dreimal geringeren Kohlenstoffablagerung führt als im Al₂O₃-stabilisierte CuO.


Im letzten Kapitel wird die Entwicklung von MgAl₂O₄-stabilisierten, Cu-modifizierten, Fe₂O₃-basierten Redoxmaterialien für die thermo-chemische Wasserspaltung beschrieben. Diese Materialien haben eine hohe Reaktivität mit CH₄ und eine niedrige Kohlenstoffablagerung. Um die Wirkung des Cu-Doping auf die signifikante Reduzierung der Kohlenstoffablagerung (wobei die hohe Redoxaktivität der Materialien nicht negativ beeinflusst wurde) besser zu verstehen, wurden detaillierte Röntgenabsorptionsfeinstrukturspektroskopie und energiedispersive Röntgenspektroskopie eingesetzt.
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Chapter 1

Introduction

1.1 Background

Economic growth and the development of today’s societies depend strongly on a reliable supply of energy. Currently, more than 80% of the global energy demand is met via the combustion of fossil fuels.\(^1\) It is very likely that, at least over the next few decades, this situation will prevail. The combustion of fossil fuels is the major source of carbon dioxide (CO\(_2\)) emissions to the atmosphere. Recently, the concentration of CO\(_2\) in the atmosphere has approached ~400 ppm, \(i.e.\) an increase of ~43% when compared to the pre-industrial value of 280 ppm.\(^2\) CO\(_2\) is arguably the dominating anthropogenic greenhouse gas and according to the Intergovernmental Panel on Climate Change (IPCC) global warming and climate change are most likely linked to its accumulation in the atmosphere.\(^3\) Without effective countermeasures and considering the increasing global energy demand, annual CO\(_2\) emissions are predicted to increase from ~32 Gt in 2012 to ~50 Gt in 2050.\(^4\) In order to limit global warming to +2 °C (compared to the pre-industrial temperature level) CO\(_2\) emissions should be reduced to ~15 Gt per year.\(^5\) In this context increased energy efficiencies, renewables, nuclear and CO\(_2\) capture and sequestration (CCS) technologies are considered to play a central role to meet ambitious CO\(_2\) emission targets.

In the concept of CCS, CO\(_2\) is captured at large point sources, compressed and subsequently stored in suitable geological formations such as saline aquifers. The overall costs of the CCS process are dominated by the CO\(_2\) capture step. For example, the costs of CO\(_2\) capture using existing technologies, \(i.e.\) physical or chemical absorption, have been estimated to be in the range of 11–91 $/t CO\(_2\).\(^6\) On the other hand, the costs for CO\(_2\) transport and storage have been calculated to be in the range 1–8 $/t CO\(_2\) and 0.5–8 $/t CO\(_2\), respectively.\(^6\) Hence, the development of less costly CO\(_2\) capture technologies is imperative if CCS is to become a viable technology for practical implementation. CO\(_2\) capture technologies can be divided into the following three architectures: (i) post-combustion,
(ii) pre-combustion and (iii) oxy-combustion CO$_2$ capture. In post-combustion CO$_2$ capture, CO$_2$ is separated from the flue gases, \textit{i.e.} after the combustion of a carbonaceous fuel in air. Amine scrubbing is a proven post-combustion CO$_2$ capture technology with regards to design and operation. However, the associated CO$_2$ capture costs, estimated to be approximately $\$55/t$ CO$_2$ are very high, potentially prohibitively high. Thus, substantial research efforts are currently being undertaken to develop alternative sorbents for post-combustion CO$_2$ capture, such as CaO-based sorbents, metal organic frameworks or zeolites. In the pre-combustion CO$_2$ capture concept a hydrocarbon is decarbonized prior to its combustion using \textit{e.g.} reforming and shift reactions. Finally, in the oxy-fuel combustion mode, oxygen (diluted with recycled CO$_2$) instead of air is used to combust a fuel. Thus, oxy-fuel combustion relies on an energy intensive and, thus, costly, air separation process.

1.1.1 Chemical looping combustion

Chemical looping combustion (CLC) is an emerging third generation CCS technology, which is conceptually linked to oxy-fuel combustion. In 1954, Lewis and Gilliland$^{12}$ first proposed CLC as a new process to produce a pure stream of CO$_2$. Subsequently, in 1983, Richter and Knoche$^{13}$ rediscovered CLC as an elegant process to reduce the thermodynamic irreversibility of the conventional combustion process. The actual term ‘CLC’ was coined in 1987 by Ishida \textit{et al.}$^{14}$ However, it took until 1994 for CLC to be considered as a highly promising approach for CO$_2$ capture.$^{15}$ CLC is a two-step process comprising a reduction and a regeneration step. In the first step, a hydrocarbon is oxidized \textit{via} lattice oxygen derived from a solid oxygen carrier, which is typically a transition metal oxide. The combustion reaction produces a mixture of CO$_2$ and steam, which can be easily separated \textit{via} condensation:

$$C_nH_{2m} + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1}$$ \hspace{1cm} (1.1)

In the regeneration step, the reduced oxygen carrier is re-oxidized with air according to:

$$2Me_xO_{y-1} + O_2 \rightarrow 2Me_xO_y$$ \hspace{1cm} (1.2)

The overall heat released in reactions 1.1 and 1.2 is equal to the value that is obtained if the same fuel would be combusted directly in air. However, unlike the conventional combustion process, a pure stream of CO$_2$ is produced inherently in CLC. Depending on the oxygen carrier, reaction 1.1 is often endothermic, whereas reaction 1.2 is always exothermic.
From a practical point of view, CLC can be operated either continuously in a circulating fluidized bed reactor or in batch mode using a single (bubbling) fluidized bed reactor. A schematic sketch of the CLC process is given in Figure 1.1.

Figure 1.1. Schematic diagram of the CLC process.

From a conceptual point of view, CLC using a gaseous fuel, e.g. methane, is a reasonably straightforward process. However, the extension of CLC to solid fuels, e.g. coal or petroleum coke, is challenging owing to (i) the very slow reaction rate of the solid-solid reaction between the fuel and the oxygen carrier and (ii) the direct contact of the oxygen carrier with the ash of the fuel. To extend CLC to solid fuels, the following two main strategies have been proposed:

1. Prior gasification of the solid fuel in oxygen or a mixture of oxygen and steam. The synthesis gas obtained is burned subsequently in the conventional CLC process for gaseous fuels. A disadvantage of this approach is the requirement of an air separation unit, which would substantially increase the CO₂ capture costs.

2. In-situ gasification of the solid fuel in the fuel reactor using recycled CO₂ or steam as the fluidizing gas. An advantage of this process configuration is that the synthesis gas obtained is immediately oxidized to CO₂ and H₂O. Thus, the reaction rate of the slow gasification reaction can be enhanced significantly (CO and H₂ are “poisons” for the
However, a disadvantage of this concept is the need to separate the unburnt fuel and the reduced oxygen carrier prior to the regeneration of the oxygen carrier in the air reactor.

1.1.2 Chemical looping with oxygen uncoupling

A general disadvantage of the CLC concepts described above is the comparatively slow gasification reaction, albeit being somewhat increased in the presence of an oxygen carrier. An attractive alternative to combust a solid fuel is chemical looping with oxygen uncoupling (CLOU). The acronym ‘CLOU’ was introduced in 2009 by Mattisson et al., however, the underlying principle of the process, i.e. the high temperature release of oxygen via the reduction reaction of a solid oxygen carrier, had already been proposed by Lewis et al. in 1951. The advantage of CLOU over CLC is that a solid fuel is directly combusted, i.e. the intermediate gasification step is generally omitted.

The first step of the CLOU process is the release of molecular oxygen through the reduction reaction of an oxygen carrier:

\[ 2\text{Me}_x\text{O}_y \rightarrow 2\text{Me}_x\text{O}_{y-1} + \text{O}_2 \]  \hfill (1.3)

Subsequently, the solid fuel reacts with oxygen to produce, after the condensation of H\textsubscript{2}O, a pure stream of CO\textsubscript{2} according to:

\[ \text{C}_n\text{H}_{2m} + (n + m/2)\text{O}_2 \rightarrow n\text{CO}_2 + m\text{H}_2\text{O} \] \hfill (1.4)

To close the cycle, the oxygen carrier is re-oxidized in air:

\[ 2\text{Me}_x\text{O}_{y-1} + \text{O}_2 \rightarrow 2\text{Me}_x\text{O}_y \] \hfill (1.5)

The main difference between CLC and CLOU is the mechanism by which the fuel is oxidized. In CLOU, gaseous fuels react not only with the molecular oxygen released by the oxygen carriers but also with lattice oxygen of the oxygen carrier, i.e. a combination of heterogeneous and homogeneous combustion reactions. On the other hand, under CLC conditions only lattice oxygen is available for the oxidation reaction, i.e. the gaseous fuel is combusted via a heterogeneous gas-solid reaction. In the case of a solid fuel, CLOU allows the direct oxidation of the fuel with molecular oxygen released by the oxygen carrier, whereas in CLC, owing to very slow solid-solid reactions, the fuel has to be gasified first to ensure a sufficiently fast rate of reaction with the solid oxygen carrier. Furthermore, in CLOU
the molecular oxygen released can also react “downstream”, e.g. in the freeboard of a fluidized bed. As a consequence, in CLOU the rate of fuel oxidation, in particular for solid fuels, is substantially increased when compared to CLC. Generally, materials for CLOU should fulfill all the requirements set for oxygen carriers for CLC, viz. high oxygen carrying capacity, being environmentally benign, high mechanical strength, fast kinetics, high resistance to attrition and agglomeration, and low cost. However, CLOU poses additional thermodynamic requirements on the oxygen carrier, i.e. the material has to release molecular oxygen at typical operating temperatures (800–1000 °C). Thus, CLOU significantly narrows the possible choices from known CLC materials.

1.1.3 Oxygen carriers for CLC and CLOU

One of the cornerstones of enabling CLC and CLOU is the development of suitable oxygen carriers. The oxygen carriers typically used for CLC are the oxides of Ni, Fe, Cu and Mn. Among these candidates, nickel oxide (NiO) has a high oxygen carrying capacity (defined as the quantity of reducible oxygen per unit weight of the oxygen carrier (OC)) of 0.21 g O₂/g OC. NiO-based oxygen carriers show a high reactivity with methane; however, Ni also catalyzes the formation of carbon effectively. Carbon formation would reduce the CO₂ capture efficiency of the CLC process, since CO₂ would be released into the atmosphere during the regeneration step. Additionally, NiO is considered to be carcinogenic. Iron oxide (Fe₂O₃) has also received significant attention for CLC applications owing to its low cost, wide availability and minimal environmental impact. However, the poor cyclability of pure, i.e. unsupported, Fe₂O₃ is currently a major drawback. It has been found that if reduced to metallic Fe, unsupported Fe₂O₃ deactivates after only a few cycles, probably due to thermal sintering. Fe₂O₃–Fe pair has the highest oxygen carrying capacity of 0.30 g O₂/g OC, however, the thermodynamic analysis of Bohn et al. showed that, under practical reducing conditions, the transformation of Fe₂O₃ to magnetite (Fe₃O₄) is favored, resulting in a low oxygen carrying capacity of Fe₂O₃ of only 0.034 g O₂/g OC. On the other hand, manganese oxide (Mn₂O₃) has received less attention for CLC applications owing to its reduction to Mn₃O₄ in air at temperatures above ~875 °C and the low oxygen carrying capacity of the Mn₂O₃–Mn₃O₄ pair (0.034 g O₂/g OC). Copper oxide (CuO) is a particularly attractive oxygen carrier for CLC owing to its exothermic reduction reactions, a high oxygen carrying capacity of 0.20 g O₂/g OC under CLC conditions, fast redox kinetics, low tendency to give carbon deposition and low toxicity. However, the low Tammann temperature of CuO (526 °C) is
a serious drawback. Besides transition metal oxides, also naturally occurring materials (such as ilmenite (FeTiO₃), Fe ores, Mn ores, Cu ores, etc.), perovskite-type oxides (e.g. CaMn₀.₈₇₅Ti₀.₁₂₅O₃₋₅ and CaMn₀.₈₅Mg₀.₁O₃₋₅) and mixed oxides (such as Mg₂MnO₄, Mn₇SiO₁₂, (MnₓFe₁₋ₓ)₂O₄, etc.) have been proposed as promising oxygen carriers for CLC.²⁹⁻³⁶

![Figure 1.2. Equilibrium partial pressure of O₂ as a function of temperature: (—) CuO/Cu₂O, (—) Mn₂O₃/Mn₃O₄ and (—) Co₃O₄/CoO. The thermodynamic data was taken from Barin and Knacke.³⁷](image)

Turning to CLOU, the first materials proposed for CLOU were CuO, Mn₂O₃ and Co₃O₄²¹, which reduce according to reaction 1.6, 1.7 and 1.8, respectively:

\[
\begin{align*}
4\text{CuO} & \leftrightarrow 2\text{Cu}_2\text{O} + \text{O}_2 & \Delta H_{900\ ^\circ\text{C}} = 257.3 \text{ kJ/mol O}_2 \\
6\text{Mn}_2\text{O}_3 & \leftrightarrow 4\text{Mn}_3\text{O}_4 + \text{O}_2 & \Delta H_{900\ ^\circ\text{C}} = 179.5 \text{ kJ/mol O}_2 \\
2\text{Co}_3\text{O}_4 & \leftrightarrow 6\text{CoO} + \text{O}_2 & \Delta H_{900\ ^\circ\text{C}} = 388.2 \text{ kJ/mol O}_2
\end{align*}
\]

The equilibrium partial pressure of O₂ as a function of temperature for reactions 1.6–1.8 is plotted in Figure 1.2. From Figure 1.2 it can be seen that for Co₃O₄, Mn₂O₃ and CuO reduction in air starts at ~780 °C, ~875 °C and ~1030 °C, respectively. Owing to its high oxygen uncoupling capacity of 0.1 g O₂/gOC, CuO is arguably also one of the most promising materials for CLOU. Importantly, the oxygen carrying capacity and the O₂ equilibrium partial
pressure of CuO can be modified by introducing, for example, Al$_2$O$_3$ or Mn$_2$O$_3$.

Besides CuO, Mn$_2$O$_3$ is also capable of releasing molecular O$_2$ in a temperature range suitable for CLOU. However, the reduction reaction of Mn$_2$O$_3$ occurs at significantly lower temperatures when compared to CuO, as shown in Figure 1.2. The main disadvantage of Mn$_2$O$_3$-based oxygen carriers is the very slow oxidation rate of Mn$_3$O$_4$.

Interestingly, metal oxides that do not possess CLOU characteristics at typical operating temperatures (800–1000 °C), such as NiO, Fe$_2$O$_3$ or SiO$_2$, undergo a reversible reduction reaction when combined with Mn$_2$O$_3$.

Turning to Co$_3$O$_4$, owing to its comparatively low reduction temperature (in air) and health concerns, Co$_3$O$_4$ is not considered commonly as a CLOU material. In addition, several perovskite-type oxides (such as CaMnO$_{3-\delta}$, CaMn$_{0.875}$Ti$_{0.125}$O$_{3-\delta}$, CaMn$_{0.9}$Mg$_{0.1}$O$_{3-\delta}$ and Ca$_x$La$_{1-x}$Mn$_{1-y}$M$_y$O$_{3-\delta}$ where M = Mg, Ti, Fe or Cu, $x = 0.9–1$ and $y = 0, 0.1$) are also able to release O$_2$ at high temperatures.

Perovskite-type materials differ from binary oxides as the equilibrium partial pressure of O$_2$ is a function of the oxygen deficiency in the perovskite structure. The oxygen carrying capacity of perovskites is also not “fixed” and depends largely on the partial pressure of O$_2$ during re-oxidation.

### 1.1.4 CuO-based oxygen carriers

From a thermodynamic point of view, CuO is arguably the most promising oxygen carrier candidate for CLC and CLOU. However, the main challenge associated with the use of CuO for CLC and CLOU, is its structural instability as the Tamman temperatures of Cu, Cu$_2$O and CuO are lower than typical operating temperatures of the CLC and CLOU processes. The Tamman temperature indicates the onset of sintering and is defined empirically as half of the melting temperature, $T_m$ (in kelvin). The Tamman temperatures of CuO, Cu$_2$O, and Cu are 526 °C, 481 °C, and 405 °C, respectively. Thus, irreversible microstructural changes are expected for CuO-based oxygen carriers during CLC and CLOU operation. To avoid the thermal sintering and agglomeration of CuO, it is commonly stabilized by a high Tamman temperature support, e.g. Al$_2$O$_3$, MgAl$_2$O$_4$, MgO or ZrO$_2$.

Over the past decade, predominantly incipient wetness impregnation, freeze granulation, spray drying and mechanical mixing techniques have been utilized to manufacture supported, CuO-based oxygen carriers for CLC and CLOU. For example, using mechanical mixing and incipient wet impregnation techniques, Gayán et al.
assessed the suitability of six different supports, viz. Al₂O₃, MgAl₂O₄, sepiolite, SiO₂, TiO₂, MgO and ZrO₂ for CuO. The CuO content and the calcination temperature were varied between 15–80 wt. % and 850–1300 °C, respectively. Initial screening experiments of the synthesized materials in the temperature range 900–1000 °C (using a thermogravimetric analyzer, TGA) revealed that Al₂O₃-, TiO₂- or SiO₂-supported oxygen carriers were not suitable for CLOU: γ-Al₂O₃- or α-Al₂O₃-supported CuO was found to have low CuO conversions irrespective of the preparation technique, CuO content and calcination temperature. This observation was explained by the formation of CuAl₂O₄ which shows very slow reduction and re-oxidation kinetics. In addition, agglomeration was identified as a serious concern for Al₂O₃- or TiO₂-supported oxygen carriers containing 80 wt. % CuO. Indeed, TiO₂-supported CuO agglomerated for CuO contents as low as 40 wt. %, possibly due to the low Tammann temperature of TiO₂ of only 789 °C. Furthermore, CuO supported on SiO₂ melted during calcination at 1100 °C, most likely due to the formation of a low melting eutectic. Further testing of the remaining oxygen carriers in a fluidized bed revealed that also MgO- and sepiolite-supported oxygen carriers are unsuitable for CLOU due to agglomeration. Ultimately, Gayán et al. identified MgAl₂O₄- and ZrO₂-supported CuO, prepared via mechanical mixing followed by pelletization and containing, respectively, 60 and 40 wt. % CuO, as the most suitable materials for CLOU. The Tammann temperatures of ZrO₂ and MgAl₂O₄ are 1214 °C and 929 °C, respectively. Interestingly, despite the higher Tammann temperature of ZrO₂, a higher weight fraction of ZrO₂ was required to manufacture agglomeration-resistant oxygen carriers. This observation indicates that the Tammann temperature of the support is not the only parameter influencing the stability and redox characteristics of the oxygen carrier, but other factors, such as the level of mixing between the active material and the support or the structure of the material, have to be considered.

Mixing between the active component, i.e. CuO, and the support on a nanometer level cannot be achieved typically with the “conventional” synthesis methods discussed above. Instead, wet-chemical synthesis approaches, such as co-precipitation or sol-gel, are required. For example, Song et al. prepared CuO-based, Al₂O₃-stabilized oxygen carriers containing 20–100 wt. % CuO via layered double hydroxide (LDH) precursors. In this study, the LDH precursors were synthesized via a co-precipitation technique. The materials were tested in a fluidized bed at 900 °C and 950 °C. The oxygen carrier containing 60 wt. % CuO showed a stable performance over more than 100 redox cycles. The high oxygen carrying capacity and excellent thermal stability of the material were attributed to the high degree of dispersion of CuO on the support. Recently, Mei et al. determined the CLOU characteristics of sol-gel
derived, CuAl$_2$O$_4$-supported CuO (60 wt. %) in the temperature range 850–950 °C. Four different coals were used as a fuel and the combustion efficiency exceeded 90 % at 900 °C, regardless of the type of coal used. However, a slight decrease in the yield of CO$_2$ with cycle number was reported.

### 1.2 Objectives of this thesis

There has been some encouraging progress in the preparation of stable, CuO-rich oxygen carriers for CLC and CLOU. However, previous studies on CuO-based oxygen carriers have mainly focused on investigating the effect of oxygen carrier composition and preparation method on its redox stability, agglomeration behavior, attrition resistance and kinetics. Nonetheless, for CuO-based materials there is currently very little understanding of the relationship between the material preparation and its structure and performance.

The aim of this thesis is to

- investigate the relationship between synthesis parameters (such as pH value and calcination temperature) and the redox characteristics of co-precipitated Al$_2$O$_3$- or MgAl$_2$O$_4$-stabilized CuO.
- probe the effect of Na$^+$ doping on the local structure and charge transport characteristics of Al$_2$O$_3$-supported CuO.
- develop CeO$_2$-$x$-stabilized CuO with very high oxygen capacity and coke resistance.
- correlate the electrical (electronic and ionic) conduction pathways to the rate of oxidation for CeO$_2$-$x$-stabilized CuO.
- assess the effect of the addition of Cu on the carbon deposition resistance of MgAl$_2$O$_4$-stabilized Fe$_2$O$_3$ for CH$_4$-based chemical looping water splitting.

The present dissertation is organized as follows.

Chapter 2 reports the development of a co-precipitation technique to prepare Al$_2$O$_3$-stabilized CuO. The influence of the co-precipitation parameters (such as the precipitation agent and pH value) on the redox characteristics of Al$_2$O$_3$-stabilized CuO was critically assessed. A detailed chemical and morphological characterization of the synthesized oxygen carriers in combination with cyclic redox measurements were used to shed light on the preparation-structure-performance relationship of the synthesized material.

In Chapter 3 the influence of the CuO content, the support material and the calcination temperature on the redox stability of the oxygen carriers is investigated. Thermogravimetric measurements were utilized to identify the synthesis parameters which
influenced the redox characteristics most. A combination of thermogravimetric and X-ray diffraction (XRD) measurements allowed us to propose a CLOU reaction mechanism for Al₂O₃-stabilized CuO.

Chapter 4 presents a Na⁺-based doping strategy to phase-stabilize Al₂O₃-supported CuO, yielding in turn a material with a high redox stability and CO₂ capture efficiency. To achieve a homogeneous distribution of the dopant (Na⁺), a sol-gel technique was employed. Utilizing in-situ and ex-situ X-ray absorption spectroscopy (XAS), the local structure of CuO and the reduction pathways of CuO were determined as a function of the Na⁺ content and cycle number. In addition, the effect of Na⁺ doping on charge transport was also probed.

Chapter 5 is concerned with the development of CeO₂ₓ-stabilized CuO for CLC and CLOU. The use of CeO₂ₓ as a support was driven by the desire to increase the oxygen capacity and coke resistance of the CuO-based oxygen carriers. The cyclic redox stability and oxygen release capacity was investigated in detail and discussed in light of the microstructure and the phase characteristics of the materials synthesized.

In Chapter 6 the effect of a CuO percolation network on the electrical properties and oxidation kinetics of CeO₂-stabilized CuO is probed. The materials synthesized were characterized using 4-point conductivity measurements, scanning electron microscopy, energy dispersive X-ray spectroscopy and temperature programmed reduction (TPR). The influence of conduction pathways and the activation energy for charge transport on the oxygen release and uptake characteristics of the oxygen carriers prepared was critically assessed and an electrical conductivity-redox performance relationship was established.

Chapter 7 is concerned with the development of MgAl₂O₄-stabilized, Cu-modified Fe₂O₃ for thermochemical water splitting that show a high reactivity with CH₄ and low rates of carbon deposition. The cyclic redox stability and water splitting characteristics were determined and interpreted in light of the morphological and phase characteristics of the material. To understand better the effect of Cu doping on reducing significantly the rate of carbon deposition (while not affecting negatively the high redox activity of the material) extended X-ray absorption fine structure spectroscopy and energy dispersive X-ray spectroscopy was employed.

Finally, Chapter 8 presents the overall conclusions of this work and gives recommendations for future work.
Chapter 2

Development of a co-precipitation technique for the synthesis of CuO-based oxygen carriers

2.1 Introduction

As outlined in Chapter 1, synthesis approaches to prepare supported oxygen carriers for CLC and CLOU have focused predominantly on mechanical mixing, freeze granulation, spray drying, and wet and dry impregnation techniques. So far, co-precipitation has not been applied frequently to synthesize oxygen carriers for CLC and CLOU. One of the major issues associated with co-precipitation is that the different ionic compounds in the solution do not necessarily precipitate out at the same pH value. Two of the few studies investigating co-precipitation to synthesize CuO-based oxygen carriers were performed by de Diego et al. and Chuang et al. de Diego et al. employed three different methods, viz. mechanical mixing (40, 60 or 80 wt. % CuO), co-precipitation (40 wt. % CuO) and impregnation (20 or 30 wt. % CuO), to synthesize SiO₂-stabilized CuO and reported that the impregnation of CuO on a support was the only successful method to synthesize oxygen carriers that possess a high reactivity and “acceptable” mechanical properties. On the other hand, Chuang et al., contradicting the results of de Diego et al., reported that Al₂O₃-stabilized CuO (20–82.5 wt. % CuO) synthesized via co-precipitation performed best. In addition, the oxygen carriers manufactured using mechanical mixing (30 or 50 wt. % CuO) or wet impregnation (21–78 wt. % CuO) were prone to agglomeration and possessed poor redox characteristics when tested in a fluidized bed reactor. Moreover, the work performed by Chuang et al. showed that the performance of the oxygen carrier synthesized via co-precipitation was affected most by the pH value at which the precipitation reaction was performed.

Considering the contradicting conclusions reported by the previous studies that have employed co-precipitation to synthesize CuO-based oxygen carriers, this Chapter is
concerned with obtaining a better understanding of the influence of the co-precipitation parameters, e.g. pH at which the precipitation is performed or the precipitation agent, on the chemical composition and morphology of the precipitated material. The redox characteristics of the calcined Al₂O₃-stabilized, CuO-based oxygen carriers, as determined in a TGA, are subsequently interpreted in light of the detailed chemical and morphological characterization of the materials synthesized.

2.2 Experimental

2.2.1 Preparation of oxygen carriers

![Figure 2.1. Titration curve of a 2 M mixed (1.5 M in Cu²⁺ and 0.5 M in Al³⁺) nitrate solution with a 2 M Na₂CO₃ solution.](image)

Al₂O₃-stabilized, CuO-based oxygen carriers were prepared using a co-precipitation technique. Two different precipitation agents, viz. NaOH and Na₂CO₃, were used and precipitation was performed for each base at four different pH values. The selection of the pH values was based on titration experiments. The titration of a 2 M mixed nitrate solution (1.5 M in Cu²⁺ and 0.5 M in Al³⁺) with a 2 M Na₂CO₃ solution is shown in Figure 2.1. As depicted in Figure 2.1, the initial addition of a few drops of the Na₂CO₃ solution into the mixed nitrate solution resulted in a sharp increase in the pH value from ~1.1 to ~2.4 without any precipitation. The precipitation of Cu²⁺ and Al³⁺ ions started at pH > 2.4 and was
completed at pH ~4.3. Once the equivalence point was reached, the further addition of Na$_2$CO$_3$ resulted in an abrupt increase in the pH of the nitrate solution from ~4.3 to ~8.8. Since Al$^{3+}$ is amphoteric, excess Na$_2$CO$_3$ results in the formation of a [Al(OH)$_4$]$^{-}$ complex which explains the relatively small, subsequent increase in pH from ~8.8 to ~10.2. Based on the acquired titration curves, co-precipitation was performed for each reagent at four different pH values: (i) before the equivalence point (pH ~3.8), (ii) near the equivalence point (pH ~5.5), (iii) in a slightly alkaline medium (pH ~8.5) and (iv) in the region of excess base solution (pH ~10.0 for Na$_2$CO$_3$ and ~11.4 for NaOH).

The ratio of the concentration of the Cu$^{2+}$ to the Al$^{3+}$ salt solutions was chosen such that the weight fraction of Al$_2$O$_3$ in the final material was ~17.5 wt. %. First a 2 M solution containing 1.5 M Cu(NO$_3$)$_2$·2.5H$_2$O and 0.5 M Al(NO$_3$)$_3$·9H$_2$O was prepared. Subsequently, a precipitating agent (2 M NaOH or Na$_2$CO$_3$) was added dropwise under magnetic stirring to the solution containing the nitrates, until the desired pH value was reached. The rate of stirring was adjusted according to the viscosity of the solution. The resulting slurry was aged for 150 min. Subsequently, the precipitate was filtered. During filtration, the precipitate was washed several times with deionized water (15 MΩ.cm at 25 °C) to remove nitrate and alkali ions. Once the electrical conductivity of the filtrate was < 25 µS/cm, the filtered precipitate was dried in an oven at 100 °C for 24 h. A sample taken from a material which was dried at 100 °C is subsequently referred to as ‘dried oxygen carrier’. The final oxygen carriers were obtained after calcination in a muffle furnace at 800 °C for 2 h using a heating rate of 5 °C/min. The calcined material was crushed and sieved into the size range of 600–710 µm. The following nomenclature will be used to characterize the synthesis protocol of the oxygen carrier. The abbreviation CuAl is followed by the precipitation agent and the pH value at which the precipitation was performed. For example, CuAl-NaOH-3.8 is an oxygen carrier which was synthesized by co-precipitation at pH ~3.8 using NaOH as the precipitating agent.

2.2.2 Characterization techniques

Dried samples were characterized using attenuated total reflection Fourier transformed infra-red (ATR-FTIR) spectroscopy and Raman spectroscopy. ATR-FTIR spectra were obtained using a Thermo Scientific Nicolet iS10 FTIR spectrometer equipped with a diamond crystal. ATR-FTIR spectra were collected by averaging 32 scans. The spectral resolution was set to 4 cm$^{-1}$. Raman spectra were acquired using a Renishaw RM 1000 Raman microscope.
equipped with a 785 nm diode laser. The samples were excited with 0.5 % of the total laser power (180 mW) for 10 s at a spectral resolution of 1 cm\(^{-1}\). Prior to the experiment, the spectrometer was calibrated using the 520.5 cm\(^{-1}\) peak of Si. For both the ATR-FTIR and the Raman spectroscopy measurements background subtraction was performed. A Bruker D8 Advance diffractometer, equipped with a Lynx eye super speed detector, was used to analyze the composition and crystallinity of (i) freshly calcined and (ii) cycled oxygen carriers. The diffractometer was operated at 40 mA and 40 kV using Cu K\(_\alpha\) radiation. Each sample was scanned in the range 20 = 20–80°. The step size was 0.0275° and the scan time per step was 0.8 s. A scanning electron microscope (FEI Quanta 200 FEG) operated at 10 kV was used to characterize the surface morphology of the dried oxygen carriers. A double-sided carbon tape was used to attach samples of the oxygen carrier onto an aluminum holder. Prior to imaging, the samples were sputter coated with an approximately 3 nm thick layer of gold. The surface area and pore volume of the synthesized oxygen carriers were determined using a Quantachrome NOVA 4000e analyzer. Prior to the acquisition of the N\(_2\) isotherms at -196 °C, each sample was degassed at 300 °C for at least 2 h. The Brunauer et al.\(^{62}\) (BET) and the Barrett et al.\(^{63}\) (BJH) models were used to calculate, respectively, the surface area and the pore volume of the freshly calcined materials from the acquired isotherms. Finally, the crushing strength of the oxygen carriers was obtained by measuring the force required to break the oxygen carrier particles (size range 1.1–2.0 mm) by using a Shimpo force gauge. Here, 15 measurements were averaged to determine the mean crushing strength of the oxygen carriers.

### 2.2.3 Performance tests

The cyclic redox performance of the oxygen carriers synthesized was evaluated in a TGA (Mettler Toledo TGA/DSC 1) by recording the weight change as a function of time and reactive gas atmosphere. Experiments performing 10 redox cycles were conducted at 800 °C. In a typical experiment, ~30 mg of an oxygen carrier was placed in an alumina pan and heated from room temperature to 800 °C at a rate of 10 °C/min under a flow of N\(_2\) (25 mL/min at 25 °C and 1 bar). The subsequent reduction step was performed using a gas mixture containing 10 vol. % CH\(_4\) in N\(_2\) (25 mL/min), whereas air (25 mL/min) was used to re-oxidize the oxygen carrier. A N\(_2\) flow (25 mL/min) was used to purge the reaction chamber for 60 s between each reaction segment. Gas switching was performed via a computer-controlled set-up containing four solenoid valves. The recorded weight changes
were used to calculate the oxygen carrying capacity ($R_o$) and fractional conversions ($X_{\text{red}}$ and $X_{\text{ox}}$), viz.:

$$R_o = \frac{m_{\text{ox}} - m_{\text{red}}}{m_{\text{ox}}}$$  \hspace{1cm} (2.1)

$$X_{\text{red}} = \frac{m_{\text{ox}} - m}{m_{\text{ox}} - m_{\text{red}}}$$  \hspace{1cm} (2.2)

$$X_{\text{ox}} = \frac{m - m_{\text{red}}}{m_{\text{ox}} - m_{\text{red}}}$$  \hspace{1cm} (2.3)

where $m_{\text{ox}}$, $m_{\text{red}}$ and $m$ are the weight of the sample in its oxidized form, the weight of the fully reduced sample and the instantaneous sample weight, respectively.

Using a TGA, the quantity of CuO in the oxygen carrier was determined using the following reaction

$$4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$$ \hspace{1cm} (2.4)

In these experiments, ~30 mg of an oxygen carrier was heated from room temperature to 1100 °C at a rate of 10 °C/min in a N$_2$ atmosphere (25 mL/min). The recorded weight change was used to determine the amount of oxygen released. The weight fraction of CuO in the original sample was calculated according to:

$$\text{Amount of CuO [wt.%]} = \frac{9.94(m_{\text{ox}} - m_{\text{red}})}{m_{\text{ox}}} \times 100$$ \hspace{1cm} (2.5)

where $m_{\text{ox}}$ and $m_{\text{red}}$ are the weight of the fully oxidized and fully reduced (in N$_2$) oxygen carrier, respectively. The conversion factor of 9.94 is obtained from the stoichiometry of reaction 2.4.
2.3 Results

2.3.1 Characterization of the dried oxygen carriers

Figure 2.2. Raman spectra of the dried oxygen carriers prepared by using different precipitating agents: (a) NaOH and (b) Na₂CO₃. Precipitation was performed at pH values of (—) 3.8, (—) 5.5, (—) 8.5, and (—) 11.4 for NaOH or 10.0 for Na₂CO₃.

Raman and ATR-FTIR spectroscopy were used to identify the composition of the dried precipitates. Figure 2.2(a) shows Raman spectra of the dried oxygen carriers precipitated at
pH 3.8, 5.5, 8.5 and 11.4 using NaOH as the precipitation agent. The Raman spectra confirm that the precipitation of a solution of nitrates of Cu$^{2+}$ and Al$^{3+}$ using NaOH as the precipitating agent resulted in the formation of gerhardtite and boehmite (AlO(OH)) for all pH values studied. Gerhardtite, Cu$_2$NO$_3$(OH)$_3$, is a basic copper(II) nitrate. The characteristic peaks of the spectra shown in Figure 2.2(a) agree well with the Raman spectrum of natural gerhardtite. The band observed in the range 3500–3600 cm$^{-1}$ with peaks located at 3510 cm$^{-1}$, 3552 cm$^{-1}$ and 3585 cm$^{-1}$ is due to the stretching of the three OH$^-$ groups of gerhardtite. The peak located at 1048 cm$^{-1}$ is assigned to the $(v_1)$ symmetric stretching mode of the NO$_3^-$ group, whereas the peaks in the range 1200–1500 cm$^{-1}$, with the main peak located at 1270 cm$^{-1}$, are due to the NO$_3^-$ ($v_3$) antisymmetric stretching vibrations. The two smaller peaks located at 645 cm$^{-1}$ and 695 cm$^{-1}$ can be assigned to the $v_4$ out of plane bending mode of the NO$_3^-$ group, whereas the three peaks located at 420 cm$^{-1}$, 390 cm$^{-1}$ and 380 cm$^{-1}$ can be attributed to the OH$^-$ deformation modes of the Cu(OH)$_3$ units. On the other hand, the broad band observed in the range 2300–2700 cm$^{-1}$ is due to the formation of boehmite.

Raman spectra of the dried oxygen carriers precipitated at pH 3.8, 5.5, 8.5 and 10.0 using Na$_2$CO$_3$ as the precipitation agent are shown in Figure 2.2(b). It was observed that boehmite was precipitated at pH 3.8 and 10.0. On the other hand, the absence of the band in the range 2300–2700 cm$^{-1}$ for the dried oxygen carrier synthesized at pH 5.5 or 8.5 indicates the precipitation of Al$^{3+}$ as gibbsite (Al(OH)$_3$). Turning to the precipitation of Cu$^{2+}$, the Raman spectrum of the dried material precipitated at pH 3.8 contains features that correspond to gerhardtite, whereas for precipitation at pH 5.5, 8.5 and 10.0, the Raman spectra of the dried oxygen carriers, precipitated using Na$_2$CO$_3$ as precipitating agent, were inconclusive. Thus, ATR-FTIR spectroscopy was performed to determine the chemical composition of these materials. The ATR-FTIR spectra of the dried oxygen carries are shown in Figure 2.3. The double peak in the region 1300–1400 cm$^{-1}$ (Figure 2.3(a)) corresponds to the asymmetric stretching of the NO$_3^-$ group, whereas the broad peak in the range 3000–3600 cm$^{-1}$ is representative of hydroxyl group stretching. Figure 2.3(a) confirms that co-precipitation using NaOH as the precipitating agent, resulted in the formation of gerhardtite independent of the pH value. This observation is in agreement with the previously described Raman spectra. The ATR-FTIR spectrum of CuAl-Na$_2$CO$_3$-3.8, Figure 2.3(b), is also representative of gerhardtite. However, performing the precipitation at pH 5.5 or higher and using Na$_2$CO$_3$ as the precipitating agent resulted in the formation of malachite. Malachite, Cu$_2$(CO$_3$)(OH)$_2$, is a basic copper(II) carbonate. In Figure 2.3(b) the broad band in the region 3000–3600 cm$^{-1}$, including a double peak, can be assigned to the hydroxyl-stretching modes of the OH$^-$ group.
of malachite, whereas the sharp peaks in the region 1350–1550 cm\(^{-1}\) can be attributed to the asymmetric C-O stretching \((\nu_3)\) of the CO\(_3^{2-}\) group of malachite.\(^6\) The sharp band at 820 cm\(^{-1}\) and the peaks in the range of 700–800 cm\(^{-1}\) are due to the out-of-plane \((\nu_2)\) and asymmetric \((\nu_4)\) bending modes of O-C-O bonds of the CO\(_3^{2-}\) group of malachite, respectively.

Figure 2.3. ATR-FTIR spectra of dried oxygen carriers synthesized by using different precipitating agents: (a) NaOH and (b) Na\(_2\)CO\(_3\). Precipitation was performed at pH (—) 3.8, (—) 5.5, (—) 8.5, and (—) 11.4 for NaOH or 10.0 for Na\(_2\)CO\(_3\).
Figure 2.4. SEM micrographs of the dried oxygen carriers: (a) CuAl-Na$_2$CO$_3$-3.8, (b) CuAl-Na$_2$CO$_3$-5.5, (c) CuAl-Na$_2$CO$_3$-8.5, (d) CuAl-Na$_2$CO$_3$-10.0, (e) CuAl-NaOH-3.8, (f) CuAl-NaOH-5.5, (g) CuAl-NaOH-8.5, and (h) CuAl-NaOH-11.4.

To probe the surface morphology of the oxygen carriers, the dried oxygen carriers were imaged using scanning electron microscopy. SEM images of the dried oxygen carriers are shown in Figure 2.4. The electron micrograph of dried CuAl-Na$_2$CO$_3$-3.8 shows platelets with an average thickness of 110 ± 30 nm and lateral size 725 ± 155 nm (Figure 2.4(a)). On the other hand, precipitation performed at pH > 5.5 using Na$_2$CO$_3$ as the precipitation
agent resulted in a different surface morphology, i.e. one showing a grainy structure. The morphology shown in Figure 2.4(b) can be considered as an intermediate of the two morphologies described above. Turning to the oxygen carriers synthesized using NaOH as the precipitating agent, Figures 2.4(e)–(h), it was found that the pH value at which the precipitation was performed strongly influenced the surface morphology. The surface of CuAl-NaOH-3.8 (Figure 2.4(e)) was comprised of tightly packed polyhedrons. The synthesis of oxygen carriers at pH 5.5 and 8.5 resulted in materials with a grainy and non-porous surface, respectively, as shown in Figures 2.4(f) and (g). Only oxygen carrier CuAl-NaOH-11.4 (Figure 2.4(h)) showed some platelet-like structures similar to CuAl-Na$_2$CO$_3$-3.8. However, the lateral size of the platelets was significantly smaller, i.e. $280 \pm 65$ nm.

2.3.2 Characterization of the freshly calcined oxygen carriers

Table 2.1 summarizes the CuO content, BET surface area, pore volume and crushing strength of the calcined oxygen carriers. It was observed that the CuO content and morphological properties of the oxygen carriers depend strongly on the pH value at which the precipitation was performed and the precipitation agent used. The crushing strength of the freshly calcined oxygen carriers was in the range of 5.3–8.3 N and was found to be highest for pH 8.5.

<table>
<thead>
<tr>
<th>Material</th>
<th>CuO content [%]</th>
<th>BET surface area [m$^2$/g]</th>
<th>BJH pore volume [cm$^3$/g]</th>
<th>Crushing strength [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAl-NaOH-3.8</td>
<td>76.4</td>
<td>33</td>
<td>0.21</td>
<td>6.2 ± 1.0</td>
</tr>
<tr>
<td>CuAl-NaOH-5.5</td>
<td>81.2</td>
<td>43</td>
<td>0.22</td>
<td>7.0 ± 1.0</td>
</tr>
<tr>
<td>CuAl-NaOH-8.5</td>
<td>81.7</td>
<td>19</td>
<td>0.18</td>
<td>8.3 ± 0.9</td>
</tr>
<tr>
<td>CuAl-NaOH-11.4</td>
<td>83.6</td>
<td>31</td>
<td>0.18</td>
<td>6.5 ± 1.0</td>
</tr>
<tr>
<td>CuAl-Na$_2$CO$_3$-3.8</td>
<td>74.2</td>
<td>27</td>
<td>0.13</td>
<td>6.9 ± 0.8</td>
</tr>
<tr>
<td>CuAl-Na$_2$CO$_3$-5.5</td>
<td>81.7</td>
<td>30</td>
<td>0.20</td>
<td>5.3 ± 0.7</td>
</tr>
<tr>
<td>CuAl-Na$_2$CO$_3$-8.5</td>
<td>82.8</td>
<td>19</td>
<td>0.17</td>
<td>7.3 ± 0.7</td>
</tr>
<tr>
<td>CuAl-Na$_2$CO$_3$-10.0</td>
<td>96.8</td>
<td>12</td>
<td>0.10</td>
<td>6.5 ± 0.7</td>
</tr>
</tbody>
</table>
Figure 2.5. X-ray diffractograms of oxygen carriers precipitated using (a) NaOH and (b) Na$_2$CO$_3$ and calcined at 800 °C for 2 h. Precipitation was performed at pH (—) 3.8, (—) 5.5, (—) 8.5, and (—) 11.4 for NaOH or 10.0 for Na$_2$CO$_3$. The following compounds were identified: (■) CuO and (●) CuAl$_2$O$_4$. 
The X-ray diffractograms of the freshly calcined oxygen carriers are shown in Figure 2.5. The only compounds identified are CuO and CuAl$_2$O$_4$; Al$_2$O$_3$ was not detected in any sample, indicating that Al$_2$O$_3$ was either present in an amorphous form or all Al$_2$O$_3$ formed with CuO the spinel CuAl$_2$O$_4$. Interestingly in CuAl-Na$_2$CO$_3$-10.0 only CuO was detected. Furthermore, only very small peaks of CuAl$_2$O$_4$ were observed in CuAl-Na$_2$CO$_3$-8.5. The absence of CuAl$_2$O$_4$ in CuAl-Na$_2$CO$_3$-10.0 can be explained by the inhibiting effect of residual Na$^+$ to spinel formation. The inhibiting effect of Na$^+$ ions to spinel formation for the CuO-Al$_2$O$_3$ system is studied in detail in Chapter 4.

2.3.3 Redox stability of the oxygen carriers

The cyclic oxygen carrying capacity of the oxygen carriers precipitated using Na$_2$CO$_3$ and NaOH as the precipitating agent is given in Figures 2.6(a) and (b), respectively. The dotted line in Figure 2.6 gives the theoretical oxygen carrying capacity of the oxygen carrier assuming full precipitation. Reduction was performed in an atmosphere containing 10 vol. % CH$_4$ in N$_2$ and re-oxidation was carried out in air. The oxygen carrying capacity of the materials synthesized depends strongly on the synthesis parameters and is in good agreement with the weight fraction of CuO in the material. For oxygen carriers synthesized using Na$_2$CO$_3$ as the precipitating agent, Figure 2.6(a), a strong influence of the pH at which precipitation was performed on the oxygen carrying capacity is observed. The materials synthesized at pH 3.8, 5.5, 8.5 and 10.0 possessed an oxygen carrying capacity of 0.139 g O$_2$/g$_{OC}$, 0.160 g O$_2$/g$_{OC}$, 0.158 g O$_2$/g$_{OC}$ and 0.109 g O$_2$/g$_{OC}$, respectively. On the other hand, CuAl-NaOH-5.5, CuAl-NaOH-8.5 and CuAl-NaOH-11.4 showed oxygen carrying capacities close to the theoretical value of 0.163 g O$_2$/g$_{OC}$. For CuAl-NaOH-3.8, the oxygen carrying capacity was 0.153 g O$_2$/g$_{OC}$. It is worth mentioning that all oxygen carriers synthesized showed stable redox behaviour. X-ray diffractograms of the cycled oxygen carriers were found to be very similar to that of the unreacted materials except for the presence of Cu$_2$O (Figure 2.7). It is likely that in the cycled materials Cu$_2$O is formed via the reduction of CuO at 800 ºC during the N$_2$ purge periods between the reduction and oxidation steps.

In order to assess the effect of cycle number on the conversion rates, Figure 2.8 plots the fractional conversion, $X$, of CuAl-NaOH-8.5 during reduction and oxidation as a function of time for the first, fifth and tenth redox cycle. As shown in Figure 2.8, the conversion rates increase from the first to the fifth cycle for both reactions. However, the conversion rates for
the tenth cycle were found to be only slightly higher than that for the fifth cycle. It is worth mentioning that for the conditions studied here, the time to reach full conversion in the reduction and oxidation reactions was very similar.

**Figure 2.6.** Cyclic oxygen carrying capacity of the materials prepared using (a) Na₂CO₃ or (b) NaOH as the precipitating base. Precipitation was performed at the following pH values: (■) 3.8, (●) 5.5, (▲) 8.5, and (♦) 10.0 for Na₂CO₃ or 11.4 for NaOH. The dashed lines correspond to the theoretical oxygen carrying capacity assuming a CuO content of 82.4 wt. % (full precipitation).
Figure 2.7. XRD patterns of the cycled oxygen carriers precipitated using (a) NaOH or (b) Na₂CO₃. Precipitation was performed at pH (—) 3.8, (—) 5.5, (—) 8.5, and (—) 11.4 for NaOH or 10.0 for Na₂CO₃. The following compounds were identified: (■) CuO, (●) CuAl₂O₄ and (▲) Cu₂O.
Figure 2.8. Effect of cycle number on the rates of fractional conversion for CuAl-NaOH-8.5 during (a) reduction and (b) oxidation reactions: (—) first cycle, (—) fifth cycle, and (—) tenth cycle.

2.4 Discussion

2.4.1 Influence of pH on CuO content and morphological properties

The surface morphology and composition of the dried oxygen carrier was affected significantly by the precipitating agent used and the pH value at which precipitation was
performed. For example, using Na$_2$CO$_3$ as the precipitating agent and precipitating at pH 3.8 resulted in the formation of gerhardtite, whereas for precipitation at pH > 3.8 the formation of malachite was favored. Dried CuAl-Na$_2$CO$_3$-3.8 possessed a platelet-like morphology (Figure 2.4(a)). On the other hand, dried oxygen carriers precipitated at pH > 3.8, Figures 2.4(b)–(d), possessed a grainy and porous texture. It is conceivable that the pores in these oxygen carriers were generated by the release of CO$_2$ during precipitation (pH > 4.5). Despite the fact that only gerhardtite was formed when precipitation was performed with NaOH, a distinct platelet-like morphology was not observed for these materials, the exception being CuAl-NaOH-11.4.

Assuming the complete precipitation of both Al$^{3+}$ and Cu$^{2+}$ from solution, the theoretical quantity of CuO in the calcined oxygen carriers is 82.4 wt. %. However, complete precipitation cannot be expected for all pH values investigated. Thus, to determine unequivocally the CuO content in the calcined oxygen carriers, oxygen uncoupling experiments were performed. Table 2.1 shows that the composition of the oxygen carriers was influenced strongly by the pH value at which precipitation was performed and weakly by the precipitating agent. For precipitation at pH 5.5 or 8.5, the composition of the oxygen carrier was close to the theoretical value of 82.4 wt. % CuO, indicating full precipitation. The CuO content of the oxygen carriers precipitated at pH 3.8 was less than 82.4 wt. %. Owing to an insufficient quantity of NaOH or Na$_2$CO$_3$ added and the lower solubility constant of Al(OH)$_3$ ($K_{sp} = 4.1 \times 10^{-33}$) compared to Cu(OH)$_2$ ($K_{sp} = 1.0 \times 10^{-9}$), Cu$^{2+}$ was precipitated out only partially for pH 3.8.$^{67}$ Precipitation at pH 10.0 resulted in the dissolution of precipitated Al$^{3+}$ compounds due to the formation of [Al(OH)$_4$]$^{-}$. Thus, the weight fraction of CuO in CuAl-Na$_2$CO$_3$-10.0 was 96.8 wt. %. The result of the oxygen uncoupling experiment of CuAl-Na$_2$CO$_3$-10.0 is in agreement with its XRD diffractogram, which shows only peaks due to CuO. In case of CuAl-NaOH-11.4, both [Al(OH)$_4$]$^{-}$ and [Cu(OH)$_4$]$^{2-}$ may form, resulting in a weight fraction of CuO close to the theoretical value.

The data summarized in Table 2.1 show that the surface area of the oxygen carriers was affected somewhat by the pH value at which precipitation was performed. This observation can be explained by the fact that the precipitation of Al$^{3+}$ at different pH values results in the formation of different polymorphs of Al$_2$O$_3$ upon calcination.$^{68}$ For both precipitating agents, the BET surface area was highest for precipitation at pH 5.5. Generally both decreasing and increasing the pH value resulted in decreasing BET surface areas, the only exception being the lower BET surface area of CuAl-NaOH-8.5 when compared to CuAl-NaOH-11.4. The observation that the surface area peaks at pH 5.5 and decreases for
pH 8.5, despite the fact that these materials contain a similar weight fraction of Al₂O₃, can be explained by the formation of a boehmite gel (AlO(OH)) at pH 5.5. Upon calcination at 800 °C, the gel is transformed into high surface area γ-Al₂O₃ whereas for the other synthesis conditions the formation of low surface area α-Al₂O₃ via a gibbsite (Al(OH)₃) intermediate is likely. The decrease of the surface area for precipitation at pH 10.0 and using Na₂CO₃ as the precipitating base can be explained by the reduced content of Al₂O₃ in this oxygen carrier. N₂ adsorption measurements of pure CuO and Al₂O₃, prepared under similar conditions, confirmed that the surface area of the mixed oxides is predominantly due to Al₂O₃. The negligible content of Al₂O₃ in CuAl-Na₂CO₃-10.0 was confirmed by the oxygen uncoupling experiments (Table 2.1).

### 2.4.2 Influence of pH on redox characteristics

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</tr>
<tr>
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</tr>
<tr>
<td>CuAl-NaOH-11.4</td>
<td>6</td>
</tr>
<tr>
<td>CuAl-Na₂CO₃-3.8</td>
<td>6</td>
</tr>
<tr>
<td>CuAl-Na₂CO₃-5.5</td>
<td>5</td>
</tr>
<tr>
<td>CuAl-Na₂CO₃-8.5</td>
<td>18</td>
</tr>
<tr>
<td>CuAl-Na₂CO₃-10.0</td>
<td>3</td>
</tr>
</tbody>
</table>

Turning to the redox characteristics of the materials synthesized, the low oxygen carrying capacity of CuAl-Na₂CO₃-3.8 can be explained by the fact that at low pH values complete precipitation is not achieved and, in turn, an Al-rich material is obtained. On the other hand, for CuAl-Na₂CO₃-5.5 and CuAl-Na₂CO₃-8.5, the quantity of lattice oxygen released during repeated redox cycles was very close to the theoretical value. This result indicates that precipitation performed at pH 5.5 and 8.5 using Na₂CO₃ as the precipitating agent resulted in the complete precipitation of Al³⁺ and Cu²⁺. This observation is in agreement with the oxygen uncoupling experiments. Furthermore, the redox measurements plotted in Figure 2.6 demonstrate that CuAl₂O₄ is fully reducible and did not have a negative impact on the oxygen carrying capacity. In the case of CuAl-Na₂CO₃-10.0, the oxygen carrying capacity decreased...
significantly due to slow reduction and oxidation kinetics. Owing to the very low quantity of Al\(_2\)O\(_3\) (3.2 wt. %) in CuAl-Na\(_2\)CO\(_3\)-10.0, agglomeration occurred during the cyclic redox operation at 800 °C, which in turn reduced appreciably the rates of the reduction and oxidation reactions. It is worth mentioning here that fixed reaction times of 15 min and 10 min were used for the reduction and oxidation reactions, respectively. On the other hand, the oxygen carriers prepared at pH 5.5, 8.5 and 11.4 using NaOH as the precipitating base yielded oxygen carrying capacities close to the theoretically expected value of a material containing 82.4 wt. % CuO. This result confirms the complete precipitation of Cu\(^{2+}\) and Al\(^{3+}\) under these conditions. For CuAl-NaOH-3.8, the oxygen carrying capacity was, due to incomplete precipitation, slightly lower than the theoretically predicted value. The oxygen carrying capacities of oxygen carriers synthesized using NaOH as the precipitating agent were in agreement with the experimentally determined weight fraction of CuO in these materials.

Furthermore, it was observed that the (apparent) rates of reduction and oxidation increased during the first five redox cycles. Wang et al.\(^{48}\) proposed that CuO-based oxygen carriers develop cracks during the initial redox cycles due to thermal stress. These cracks increase the surface area and pore volume of the material and, thus, also the rates of conversion. Wang et al.\(^{48}\) also demonstrated that the structural and morphological properties of the oxygen carrier stabilized after a few cycles of operation. In this work, it was found that the BET surface area of the cycled oxygen carriers decreased after 25 redox cycles, the only exception being the oxygen carriers synthesized at pH 8.5 (see Table 2.2). Moreover, the lower surface area of the cycled materials did not seem to have a detrimental effect on the redox stability of the material (Figure 2.6). Therefore, the increase in the (apparent) rate of reduction and oxidation with cycle number cannot be linked with an increase in the surface area. The effect of cycle number on redox kinetics will be discussed in detail in Chapter 4.

### 2.5 Conclusions

CuO-based, Al\(_2\)O\(_3\)-stabilized oxygen carriers were prepared using a co-precipitation technique. Co-precipitation was performed at four different pH values, i.e. 3.8, 5.5, 8.5, and 10.0 for Na\(_2\)CO\(_3\) and 11.4 for NaOH. The dried oxygen carriers were characterized by Raman and ATR-FTIR spectroscopy. It was found that gerhardtite is formed at all four pH values when NaOH is used as the precipitating agent. However, using Na\(_2\)CO\(_3\) as the precipitation agent, gerhardtite is only formed at pH 3.8, whereas at all other pH values the formation of
malachite was observed. Using SEM analysis it was demonstrated that precipitating with NaOH favoured the formation of compact, dense structures, whereas grainy and more porous structures were formed for precipitation at pH ≥ 5.5 using Na₂CO₃ as the precipitating agent. N₂ adsorption analysis revealed that precipitation at pH 5.5 yielded materials with the highest surface areas independent of the precipitating agent. With regards to redox characteristics, it was shown that the oxygen carrying capacity of all oxygen carriers synthesized here remained stable over 10 redox cycles. Furthermore, it was found that CuO present in the form of CuAl₂O₄ is fully reducible. Therefore, the formation of CuAl₂O₄ did not reduce the oxygen carrying capacity of the materials. The oxygen carriers synthesized at pH 5.5 and 8.5 using NaOH or Na₂CO₃ as the precipitating agent were determined to be the best oxygen carriers for CLC using methane as a fuel owing to their high and stable oxygen carrying capacity.
Chapter 3

Structure-property relationship of co-precipitated CuO-based, Al$_2$O$_3$- or MgAl$_2$O$_4$-stabilized oxygen carriers for CLOU

3.1 Introduction

In Chapter 2 it was demonstrated that it is possible to synthesize Al$_2$O$_3$-stabilized, CuO-based oxygen carriers with excellent mechanical properties, high oxygen carrying capacity and stable redox performance by judiciously choosing the pH value at which the precipitation was performed. In this Chapter, the influence of the CuO content, the support material and the calcination temperature on the redox stability of oxygen carriers, synthesized via co-precipitation, is studied systematically. The oxygen carriers were characterized in detail using XRD, TPR, N$_2$ adsorption, scanning electron microscopy and thermogravimetric analysis to elaborate a synthesis-performance relationship. An important aspect of this work was the determination of the maximal CuO content in the oxygen carriers that allowed a stable CLOU performance.

3.2 Experimental

3.2.1 Oxygen carrier synthesis

CuO-based, MgAl$_2$O$_4$- or Al$_2$O$_3$-stabilized oxygen carriers were synthesized using co-precipitation. Precipitation was performed at pH 10.0 and 8.5 for MgAl$_2$O$_4$- and Al$_2$O$_3$-supported oxygen carriers, respectively. NaOH was used as the precipitating base. The synthesis protocol comprised the following steps. First, a 2 M aqueous solution containing Cu(NO$_3$)$_2$·2.5H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Mg(NO$_3$)$_2$·6H$_2$O (or Cu(NO$_3$)$_2$·2.5H$_2$O and Al(NO$_3$)$_3$·9H$_2$O) was prepared. The amounts of Cu$^{2+}$, Al$^{3+}$ and Mg$^{2+}$ nitrate (or Cu$^{2+}$ and
Al\(^{3+}\) nitrate) were adjusted such that the calcined oxygen carriers contained 70, 80 or 90 wt. % CuO. Subsequently, a 2 M NaOH solution was added dropwise to 100 mL of the nitrate solution under magnetic stirring. Once a pH value of 10.0 (or 8.5) was reached, the resulting slurry was aged for 150 min at room temperature. To remove excess Na\(^+\) and nitrate ions, the precipitate was washed several times with deionized water (15 MΩ cm at 25 °C). Once the electrical conductivity of the filtrate was ~200 μS/cm, the precipitate was dried in an oven at 100 °C for 24 h. Subsequently, the dried material was calcined in a muffle furnace at two different temperatures, viz. 800 °C or 1000 °C, for 2 h using a heating rate of 5 °C/min. The quantity of the calcined oxygen carrier obtained was approximately 15 g. Finally, the calcined oxygen carrier was crushed and sieved into the size range 300–425 μm. The following nomenclature is used to characterize the synthesis protocol of the oxygen carrier: the symbol Cu is followed by the weight percentage of CuO, an abbreviation for the support material (i.e. MgAl or Al) and the temperature at which the oxygen carrier was calcined. For example, Cu70MgAl-800 is an MgAl\(_2\)O\(_4\)-stabilized oxygen carrier that contains 70 wt. % CuO and was calcined at 800 °C.

3.2.2 Material characterization

The surface area and pore volume of the unreacted oxygen carriers were determined using N\(_2\)-physisorption (Quantachrome NOVA 4000e analyzer). The Brunauer et al.\(^{62}\) (BET) and Barrett et al.\(^{63}\) (BJH) models were used to calculate the surface area and pore volume, respectively. Prior to the acquisition of the N\(_2\) isotherms the oxygen carriers were degassed at 300 °C for at least 2 h. The mechanical strength of the unreacted oxygen carriers was determined by measuring the force required to break the oxygen carrier particles (size range 300–425 μm) using a Shimpo breaking force gauge. To obtain a representative value for the crushing strength, 20 particles were tested.

A Bruker AXS D8 Advance X-ray diffractometer was used to acquire powder XRD patterns of the unreacted and cycled oxygen carriers. The diffractometer was mounted with a Lynx eye super speed detector and operated at 40 kV and 40 mA using Cu K\(_\alpha\) radiation. Each sample was scanned within the range of 2θ = 20–80° with a step size of 0.0275° per second. High resolution scanning electron microscopy (HR-SEM) and energy dispersive X-ray (EDX) spectroscopy was used to morphologically characterize the calcined oxygen carriers (Zeiss LEO 1530 FEG). The samples were sputter coated with platinum before imaging. To determine the content of CuO and the reduction characteristics of the
oxygen carriers synthesized, N₂-TPR experiments were performed using a TGA (Mettler Toledo TGA/DSC 1). In a typical experiment, a small amount (~30 mg) of oxygen carrier was heated from room temperature to 1150 °C at a rate of 10 °C/min under a flow of N₂ of 100 mL/min. In all experiments, a constant N₂ flow of 25 mL/min was used as purge flow over the micro-balance.

### 3.2.3 Cyclic CLOU characteristics

The cyclic CLOU performance of the oxygen carriers was studied in a TGA at 950 °C. In a typical experiment, a fixed amount of an oxygen carrier (~30 mg) was loaded in an alumina pan and heated to 950 °C at a rate of 10 °C/min under a flow of N₂ (25 mL/min at 25 °C and 1 bar). Once the reaction temperature was reached, the oxygen carrier was allowed to reduce for 20 min in a N₂ flow of 25 mL/min. Subsequently, the N₂ flow was stopped and the material was re-oxidized for 20 min in air (25 mL/min). A constant N₂ flow of 25 mL/min was used as purge flow over the microbalance. For each oxygen carrier, ten CLOU cycles were performed. The oxygen uncoupling capacity (\( R \)) and the fractional conversion (\( X_{\text{red}} \)) were calculated from the continuously recorded weight change using, respectively, equation 3.1 and 3.2:

\[
R = \frac{m_{\text{ox}} - m_{\text{red}}}{m_{\text{ox}}} \quad (3.1)
\]

\[
X_{\text{red}} = \frac{m_{\text{ox}} - m}{m_{\text{ox}} - m_{\text{red}}} \quad (3.2)
\]

Here \( m_{\text{ox}} \), \( m_{\text{red}} \) and \( m \) are the weight of the oxygen carrier at the start of the reduction step (i.e. when it is fully oxidized), the weight of the oxygen carrier at the end of the reduction step (i.e. when it is fully reduced in N₂) and the instantaneous sample weight, respectively.

The cyclic CLOU performance of the oxygen carriers calcined at 1000 °C was also evaluated in a fluidized bed operated at 950 °C. Detailed information on the experimental set-up can be found in the Appendix A1.1. The experimental protocol to study the cyclic reduction and re-oxidation reactions in a fluidized bed was as follows: a batch of 20 g Al₂O₃ (300–425 µm) comprised the bulk of the fluidized bed. The bed was fluidized by N₂ using a flow rate of 3 L/min (25 °C and 1 bar; \( U/U_{\text{mf}} = 4.4 \)) and was operated at 950 °C. Once the operating temperature was reached, 1 g of the oxygen carrier was added to the fluidized bed.
and 25 CLOU cycles were performed. The duration of the reduction and re-oxidation reactions were fixed to 120 s and 180 s, respectively. The flow rate of the inlet gas was set to 3 L/min, as measured at 25 °C and 1 bar, in each segment of a cycle. The moles of O\textsubscript{2} produced during the CLOU reaction were calculated according to:

\[ N_{O_2} = V_{N_2} \times \int \frac{y_{O_2}}{1 - y_{O_2}} \, dt \]  

(3.3)

where \( N_{O_2} \) is the number of moles of O\textsubscript{2} produced in each cycle, \( V_{N_2} \) is the molar flow rate of N\textsubscript{2} and \( y_{O_2} \) is the mole fractions of O\textsubscript{2} in the off-gases. At the end of the experiment, the reactor was cooled down to room temperature and the cycled oxygen carrier was recovered for XRD analysis. Assuming complete reduction of the oxygen carriers (containing theoretically 70, 80 or 90 wt. % CuO) the normalized yield of O\textsubscript{2} was calculated as follows:

\[
\text{Normalized yield of O}_2 = \frac{\text{measured amount of O}_2 \text{ released}}{\text{theoretical amount of O}_2 \text{ released}}
\]  

(3.4)

### 3.3 Results

#### 3.3.1 XRD and N\textsubscript{2}-TPR analysis

XRD measurements were performed to determine the influence of the calcination temperature on the crystallinity and the chemical composition of the synthesized materials. The X-ray diffractograms of the Al\textsubscript{2}O\textsubscript{3}- and MgAl\textsubscript{2}O\textsubscript{4}-stabilized oxygen carriers are given in Figures 3.1(a) and (b), respectively. Figure 3.1(a) shows only the presence of CuO and CuAl\textsubscript{2}O\textsubscript{4} in Al\textsubscript{2}O\textsubscript{3}-stabilized oxygen carriers, independent of the calcination temperature. CuAl\textsubscript{2}O\textsubscript{4} is a mixed oxide of CuO and Al\textsubscript{2}O\textsubscript{3} and has a cubic spinel structure. Al\textsubscript{2}O\textsubscript{3} was not detected in the CuO-Al\textsubscript{2}O\textsubscript{3} oxygen carriers, indicating that either all Al\textsubscript{2}O\textsubscript{3} formed CuAl\textsubscript{2}O\textsubscript{4} or Al\textsubscript{2}O\textsubscript{3} was present in an amorphous form. On the other hand, independent of the calcination temperature, MgAl\textsubscript{2}O\textsubscript{4}-stabilized oxygen carriers only contained CuO and MgAl\textsubscript{2}O\textsubscript{4}, as shown in Figure 3.1(b). Unlike for Al\textsubscript{2}O\textsubscript{3}-stabilized materials, the formation of mixed oxides between the active compound, i.e. CuO, and the support, i.e. MgAl\textsubscript{2}O\textsubscript{4}, Al\textsubscript{2}O\textsubscript{3} or MgO, was not observed for MgAl\textsubscript{2}O\textsubscript{4}-stabilized oxygen carriers. Using XRD the presence of alumina or magnesia could not be detected indicating that all Al\textsubscript{2}O\textsubscript{3} and MgO formed MgAl\textsubscript{2}O\textsubscript{4} or existed in amorphous phases. The increase of the intensity and the decrease of the full width at half maximum of the diffraction peaks of the oxygen carriers calcined at
1000 ºC, when compared to materials calcined at 800 ºC, indicates an increase in crystallinity and/or the growth of the size of the crystallites with increasing temperature.\textsuperscript{69-71} The average crystallite size of the synthesized oxygen carriers, estimated using Scherrer’s equation\textsuperscript{72}, is given in Table 3.1.

Table 3.1. Average crystallite size of CuO, CuAl\textsubscript{2}O\textsubscript{4} and MgAl\textsubscript{2}O\textsubscript{4} in the oxygen carriers synthesized. The average crystallite sizes were calculated from the 200, 311 and 311 planes of, respectively, CuO, CuAl\textsubscript{2}O\textsubscript{4} and MgAl\textsubscript{2}O\textsubscript{4}.

<table>
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<th>Material</th>
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<th>CuAl\textsubscript{2}O\textsubscript{4} [nm]</th>
<th>MgAl\textsubscript{2}O\textsubscript{4} [nm]</th>
<th>CuO [nm]</th>
<th>CuAl\textsubscript{2}O\textsubscript{4} [nm]</th>
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Figure 3.1. XRD patterns of (a) Al\textsubscript{2}O\textsubscript{3}- and (b) MgAl\textsubscript{2}O\textsubscript{4}-stabilized, CuO-based oxygen carriers. The oxygen carriers were calcined at two different temperatures, viz. 800 °C and 1000 °C. The following compounds were identified: (▲) CuO, (■) CuAl\textsubscript{2}O\textsubscript{4} and (●) MgAl\textsubscript{2}O\textsubscript{4}.
Figure 3.2. $\text{N}_2$-TPR profiles of $\text{Al}_2\text{O}_3$-stabilized oxygen carriers containing (---) 70 wt. %, (—) 80 wt. % or (—) 90 wt. % CuO. The oxygen carriers were calcined at (a) 800 ºC and (b) 1000 ºC. The solid and the dashed vertical lines correspond to the temperatures at which the weight loss is 1 % and 98 % of the total weight change, respectively.

To determine the influence of the calcination temperature and the CuO content on the thermal reduction characteristics of the oxygen carriers synthesized, $\text{N}_2$-TPR experiments were performed. Figures 3.2 and 3.3 plot the normalized weight loss as a function of temperature for $\text{Al}_2\text{O}_3$- and $\text{MgAl}_2\text{O}_4$-stabilized oxygen carriers, respectively. The data in Figure 3.2 show that the calcination temperature and the CuO content in the oxygen carrier have a strong effect on the reduction characteristics of $\text{Al}_2\text{O}_3$-stabilized materials owing to
the interaction of CuO with Al$_2$O$_3$. The reduction of CuO-Al$_2$O$_3$ oxygen carriers calcined at 800 °C occurred in the temperature range 735–970 °C via a single step mechanism, irrespective of the CuO content. However, it can be seen from Figure 3.2(a) that for temperatures exceeding 930 °C, the reduction rates of the oxygen carriers were very slow. This is probably due to the slow reduction of CuAl$_2$O$_4$ present in the oxygen carriers. On the other hand, the reduction of oxygen carriers calcined at 1000 °C occurred in the temperature range 770–1050 °C and revealed a clear two step reduction mechanism for Cu$_80$Al$_{1000}$ and Cu$_90$Al$_{1000}$. In the first reduction step (770–950 °C), bulk CuO forms Cu$_2$O. The comparatively slow reduction of CuAl$_2$O$_4$ to CuAlO$_2$ occurred in a second step in the temperature range 950–1050 °C. A kink in the normalized mass loss curve of Cu$_{70}$Al$_{1000}$ at ~985 °C suggests that also the reduction of Cu$_{70}$Al$_{1000}$ occurred in two steps. However, the initial rate of reduction of Cu$_{70}$Al$_{1000}$ was slow compared to the other two oxygen carriers calcined at 1000 °C. This behavior can be explained by the diminished amount of bulk CuO in Cu$_{70}$Al$_{1000}$. Assuming that all Al$_2$O$_3$ in Cu$_{70}$Al$_{1000}$ reacts with CuO, the quantity of bulk CuO would be only 46.6 wt. %. Thus the dominant phase in Cu$_{70}$Al$_{1000}$ is CuAl$_2$O$_4$ and not CuO. The N$_2$-TPR results indicate that CuAl$_2$O$_4$ does not only possess slow reduction kinetics, but CuAl$_2$O$_4$ also influences negatively the rate of reduction of bulk CuO, probably due to both kinetic and thermodynamic effects.

![Table 3.2](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>CuO content [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{70}$Al$</em>{1000}$</td>
<td>71</td>
</tr>
<tr>
<td>Cu$<em>{80}$Al$</em>{1000}$</td>
<td>80</td>
</tr>
<tr>
<td>Cu$<em>{90}$Al$</em>{1000}$</td>
<td>91</td>
</tr>
<tr>
<td>Cu$<em>{70}$MgAl$</em>{1000}$</td>
<td>72</td>
</tr>
<tr>
<td>Cu$<em>{80}$MgAl$</em>{1000}$</td>
<td>81</td>
</tr>
<tr>
<td>Cu$<em>{90}$MgAl$</em>{1000}$</td>
<td>88</td>
</tr>
</tbody>
</table>

Turning to MgAl$_2$O$_4$-stabilized oxygen carriers, it was found that only the calcination temperature affected the reduction characteristics. As shown in Figure 3.3(a), the reduction of the oxygen carriers calcined at 800 °C started at ~730 °C and was completed at ~945 °C. For oxygen carriers calcined at 1000 °C, the temperature range over which the reduction reaction occurred shifted to slightly higher temperatures, i.e. to 780–970 °C. The total amount
of CuO (both in its pure form and in the form of CuAl$_2$O$_4$) in the synthesized oxygen carriers, as determined from the weight loss during the reduction reaction, is summarized in Table 3.2. For all oxygen carriers the N$_2$-TPR determined CuO contents were close to the theoretically expected values.

![Graph](image)

**Figure 3.3.** N$_2$-TPR profiles of MgAl$_2$O$_4$-stabilized oxygen carriers containing (—) 70 wt. %, (—) 80 wt. % or (—) 90 wt. % CuO. The oxygen carriers were calcined at (a) 800 °C or (b) 1000 °C. The solid and the dashed vertical lines correspond to the temperatures at which the weight loss is 1 % and 98 % of the total weight change, respectively.
3.3.2 Structural characterization

Table 3.3 summarizes the BET surface area, the BJH pore volume and the crushing strength of the oxygen carriers synthesized as a function of (i) the CuO content, (ii) the calcination temperature and (iii) the support material. The crushing strength of the oxygen carriers calcined at 800 °C was in the range of 1.4–3.5 N, irrespective of the support. As expected, increasing the calcination temperature to 1000 °C increased the crushing strength of the materials (2.5–5.7 N). The BET surface area and the BJH pore volume of the oxygen carriers calcined at 800 °C was in the range of 20–30 m²/g and 0.12–0.17 cm³/g, respectively. Upon calcination at 1000 °C, a drastic decrease in the surface area and pore volume was observed. With the exception of Cu70Al-1000 (surface area of 9 m²/g), the surface area of all oxygen carriers was ≤ 2 m²/g. The measurements summarized in Table 3.3 indicate that the content of CuO and the type of support, *i.e.* Al₂O₃ or MgAl₂O₄, had no significant influence on the surface area, pore volume and crushing strength of the oxygen carriers. Indeed, the structural properties of the synthesized oxygen carriers were influenced only by the calcination temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area [m²/g]</th>
<th>BJH pore volume [cm³/g]</th>
<th>Crushing strength [N]</th>
<th>BET surface area [m²/g]</th>
<th>BJH pore volume [cm³/g]</th>
<th>Crushing strength [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu70Al</td>
<td>30</td>
<td>0.17</td>
<td>2.7</td>
<td>9</td>
<td>0.05</td>
<td>5.7</td>
</tr>
<tr>
<td>Cu80Al</td>
<td>20</td>
<td>0.16</td>
<td>1.5</td>
<td>2</td>
<td>0.02</td>
<td>4.4</td>
</tr>
<tr>
<td>Cu90Al</td>
<td>20</td>
<td>0.17</td>
<td>1.4</td>
<td>&lt; 0.5</td>
<td>0.01</td>
<td>2.5</td>
</tr>
<tr>
<td>Cu70MgAl</td>
<td>32</td>
<td>0.12</td>
<td>3.5</td>
<td>&lt; 0.5</td>
<td>0.05</td>
<td>4.8</td>
</tr>
<tr>
<td>Cu80MgAl</td>
<td>26</td>
<td>0.15</td>
<td>2.6</td>
<td>1</td>
<td>0.01</td>
<td>4.7</td>
</tr>
<tr>
<td>Cu90MgAl</td>
<td>30</td>
<td>0.12</td>
<td>2.4</td>
<td>1</td>
<td>0.01</td>
<td>4.1</td>
</tr>
</tbody>
</table>

The surface morphology of the oxygen carriers calcined at 1000 °C was imaged using HR-SEM. The electron micrographs are shown in Figure 3.4 and indicate that the surface morphology of the oxygen carriers was strongly influenced by the support material. For example, Cu90Al-1000 possessed a morphology comprised of platelets. The average
lateral size and thickness of a platelet was $0.9 \pm 0.2 \, \mu m$ and $219 \pm 45 \, nm$, respectively. Using EDX analysis, the platelets were found to be composed of CuO. EDX analysis further revealed that CuAl$_2$O$_4$ (or Al$_2$O$_3$) were present in the form of nanometer-sized grains on the surface of the CuO platelets. The CuAl$_2$O$_4$ particles covering the platelets have an average size of $75 \pm 14 \, nm$ and formed agglomerates instead of being homogeneously distributed. On the other hand, the surface of Cu90MgAl-1000 comprised of tightly packed polyhedrons and was uniformly covered with MgAl$_2$O$_4$ particles as shown in Figure 3.4(b). The average size of the MgAl$_2$O$_4$ particles was $48 \pm 7 \, nm$. Some local sintering of CuO was also observed for Cu90MgAl-1000.

![Figure 3.4.](image)

**Figure 3.4.** High resolution scanning electron micrographs of the oxygen carriers synthesized: (a) Cu90Al-1000 and (b) Cu90MgAl-1000.
3.3.3 Thermogravimetric analysis

![Graph](image)

**Figure 3.5.** Cyclic oxygen uncoupling capacity as determined in a TGA at 950 °C: (a) Al$_2$O$_3$- and (b) MgAl$_2$O$_4$-supported oxygen carriers. Open symbols correspond to the oxygen carriers calcined at 800 °C and containing (○) 70, (△) 80 and (□) 90 wt. % CuO. Filled symbols represent the oxygen carriers calcined at 1000 °C and containing (●) 70, (▲) 80 and (■) 90 wt. % CuO.

To determine the influence of the calcination temperature, the support material, and the CuO content on the CLOU characteristics, the cyclic oxygen uncoupling capacity, $R$, was determined from TGA experiments performed at 950 °C. The cyclic oxygen uncoupling capacity of Al$_2$O$_3$- and MgAl$_2$O$_4$-stabilized oxygen carriers is plotted in Figure 3.5(a) and (b),
respectively. All Al2O3-stabilized oxygen carriers revealed a substantial decrease in the amount of oxygen released over the first 3–4 cycles. The extent of the reduction of the oxygen uncoupling capacity over the initial cycles was found to decrease with increasing CuO content. Al2O3-stabilized oxygen carriers containing 70, 80 and 90 wt. % CuO showed a decrease in their oxygen carrying capacities by, respectively, ~62, ~32 and ~12 % over 10 CLOU cycles. From Figure 3.5(a) it can be seen that the calcination temperature did not affect the CLOU characteristics substantially. On the other hand, MgAl2O4-stabilized oxygen carriers possessed a high and stable oxygen uncoupling capacities over the 10 cycles tested, irrespective of the CuO content and the calcination temperature (Figure 3.5(b)).

3.3.4 Fluidized bed experiments

![Figure 3.6](image)

**Figure 3.6.** Concentration profile of O2 release during the first decomposition step: (—) Cu80Al-1000 and (—) Cu80MgAl-1000. The experiment was performed at 950 °C in a fluidized bed. The blue line (—) plots the oxygen concentration during a blank experiment, whereas the horizontal dotted line (········) corresponds to the equilibrium oxygen concentration at 950 °C.

The CLOU performance of the oxygen carriers calcined at 1000 °C was also evaluated in a fluidized bed operated at 950 °C. The reduction reaction was performed in a N2 atmosphere, whereas a mixture of 10.5 vol. % O2 and 89.5 vol. % N2 was used for re-oxidation. Here, it should be noted that a high temperature in the fuel reactor would enhance the rate of fuel
combustion owing to the higher equilibrium partial pressure of O₂. A high temperature in the air reactor would, on one hand, decrease the driving force for Cu oxidation, but on the other hand increase the rate constant of the oxidation reaction (assuming Arrhenius-type rate law). As depicted in Figure 3.6, the concentration of O₂ during decomposition was close to the equilibrium O₂ concentration. At the beginning of the reduction step the O₂ concentration decreased, from 4.1 mol/m³ to 1.6 mol/m³, similar to a blank experiment. The reduction of Cu80Al-1000 and Cu80MgAl-1000 started once the oxygen concentration in the fluidized bed was close to the equilibrium O₂ concentration, i.e. ~1.6 mol/m³. The continuous decrease in the O₂ concentration, as observed in Figure 3.6, was due to the fact that only 1 g of oxygen carrier was used in the fluidized bed measurements. Nonetheless, Figure 3.6 demonstrates that both Al₂O₃- and MgAl₂O₄-stabilized oxygen carries were capable of providing an O₂ atmosphere close to equilibrium.

Figure 3.7. Normalized yield of O₂ as determined from fluidized bed experiments at 950 °C. The oxygen carriers were calcined at 1000 °C. The duration of the reduction and re-oxidation reaction was fixed to 120 s and 180 s, respectively. Open symbols correspond to the MgAl₂O₄-stabilized oxygen carriers containing (○) 70, (△) 80 and (■) 90 wt. % CuO, whereas filled symbols denote the Al₂O₃-stabilized oxygen carriers containing (●) 70, (▲) 80 and (■) 90 wt. % CuO.

Figure 3.7 shows the yield of O₂ as a function of cycle number for Al₂O₃- and MgAl₂O₄-stabilized oxygen carriers. It can be seen that all Al₂O₃-stabilized oxygen carriers
gave O₂ yields less than unity. For Cu70Al-1000, an increase in the yield of O₂ was observed during the initial cycles. The O₂ concentration profile revealed that complete reduction of Cu70Al-1000 was not achieved during the first cycle. However, the rate of reduction of Cu70Al-1000 increased with cycle number, resulting in an increase in the O₂ yield. The increase in the rate of reduction with cycle number will be discussed in detail in Chapter 4. After 10 cycles, the O₂ yield of Cu70Al-1000 started to decrease. On the other hand, for Cu80Al-1000 and Cu90Al-1000, the O₂ yields decreased continuously with cycle number.

To elucidate the reason for the decrease in O₂ yield for Al₂O₃-supported oxygen carriers, X-ray diffractograms were made of the cycled oxygen carriers (Figure 3.8). The diffractograms showed the presence of CuAlO₂ and CuAl₂O₄ in the cycled oxygen carriers. This would indicate that CuAlO₂ is not oxidized fully back to CuAl₂O₄ under the conditions studied here, thus leading to a reduced oxygen carrying capacity for Al₂O₃-supported CuO. From an equilibrium thermodynamics point of view, the O₂ partial pressure used, i.e. \( p_{O_2} = 0.105 \), is sufficient to re-oxidize CuAlO₂ back to CuAl₂O₄, thus indicating kinetic limitations for the re-oxidation of CuAlO₂ to CuAl₂O₄. The low O₂ yields of Al₂O₃-supported oxygen carriers further suggest that the presence of CuAl₂O₄ (or CuAlO₂) lowered the reduction kinetics of bulk CuO. These results are in agreement with the N₂-TPR results of Al₂O₃-stabilized oxygen carriers calcined at 1000 °C. Turning now to MgAl₂O₄-stabilized oxygen carriers, both Cu70MgAl-1000 and Cu80MgAl-1000 showed high and stable O₂ yields over the 25 cycles tested. Over the first 22 cycles, the O₂ yield of Cu90MgAl-1000 was equal to unity but started to decrease subsequently, possibly due to attrition. This observation would indicate that 10 wt. % MgAl₂O₄ is not sufficient to mechanically stabilize CuO for fluidized bed operations. The XRD patterns of the cycled materials confirmed that the composition of the oxygen carriers was preserved over 25 cycles, i.e. only CuO and MgAl₂O₄ were detected.
3.4 Discussion

3.4.1 Synthesis-performance relationship

An important aspect of this work was to establish a synthesis-performance relationship for the oxygen carriers synthesized. It was found that the phases present in the oxygen carriers...
were not affected by the calcination temperatures (Figure 3.1). For Al₂O₃-stabilized oxygen carriers, this observation is in agreement with the phase diagram of the Cu₂O-CuO-Al₂O₃ system which indicates the formation of the CuAl₂O₄ spinel at both 800 °C and 1000 °C. However, from Figures 3.2 and 3.3 it is evident that the calcination temperature of the oxygen carriers had a significant influence on the oxygen release characteristics of the materials. For example, an increase in the calcination temperature resulted in an increase in the reduction temperature of CuO. In addition, the apparent rate of the reduction reaction decreased with increasing calcination temperature. It is conceivable that the increase in the crystallite size with increasing calcination temperature (Table 3.1) decreased the O²⁻ mobility in the material. The influence of O²⁻ transport characteristics on the redox kinetics will be discussed in more detail in Chapter 6. As expected, the mechanical strength of the oxygen carriers increased with increasing calcination temperatures, however, at the cost of a decrease in both surface area and pore volume. A sufficiently high mechanical strength of the oxygen carriers is particularly important for fluidized bed operations. Moreover, as shown previously in section 2.4.2, a low surface area and pore volume did not affect negatively the redox characteristics of the oxygen carrier. To summarize, the surface area, pore volume, crushing strength, degree of crystallinity and extent of interaction between the support and the active phase can be adjusted by a judicious choice of the calcination temperature.

3.4.2 CLOU reaction mechanism of Al₂O₃-stabilized oxygen carriers

The oxygen carrying capacity of Al₂O₃-stabilized oxygen carriers was found to decrease continuously with cycle number when tested at 950 °C in a TGA. The decrease in the quantity of O₂ released can be explained via the following reaction mechanism: In the first cycle, bulk CuO and CuAl₂O₄ decompose via

\[ 4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2 \]  
\[ 4\text{CuAl}_2\text{O}_4 \rightarrow 4\text{CuAlO}_2 + 2\text{Al}_2\text{O}_3 + \text{O}_2, \]

respectively. In the regeneration step, all Cu₂O is re-oxidized back to CuO:

\[ 2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO} \]
whereas only a small quantity of the CuAlO$_2$ is converted back to CuAl$_2$O$_4$ owing to the slow oxidation kinetics of CuAlO$_2$:

$$4\text{CuAlO}_2 + 2\text{Al}_2\text{O}_3 + \text{O}_2 \rightarrow 4\text{CuAl}_2\text{O}_4 \quad (3.8)$$

In addition, some Al$_2$O$_3$, formed via reaction 3.6, reacts with CuO to form CuAl$_2$O$_4$:

$$\text{Al}_2\text{O}_3 + \text{CuO} \rightarrow \text{CuAl}_2\text{O}_4 \quad (3.9)$$

As a consequence, the oxygen carrying capacity decreases with cycle number, since bulk CuO forms CuAl$_2$O$_4$ which is irreversibly decomposed to CuAlO$_2$ and Al$_2$O$_3$. Reactions 3.5–3.9 continue to occur until Al$_2$O$_3$ has been fully converted to CuAlO$_2$. Based on the proposed reaction scheme, a decrease in the theoretical oxygen carrying capacity by 16 %, 37 % and 65 % for oxygen carriers containing, respectively, 10, 20 and 30 wt. % Al$_2$O$_3$, would be expected. Indeed a reduction in the oxygen carrying capacity by 12 %, 32 % and 62 % was observed after 10 cycles for oxygen carriers containing, respectively, 90 wt. %, 80 wt. % and 70 wt. % CuO. A possible strategy to circumvent this loss in oxygen carrying capacity would be the complete reduction of CuO to Cu prior to the re-oxidation step. However, at the same time this would increase the risk of agglomeration for CuO-rich oxygen carriers. Alternatively, the formation of the CuAl$_2$O$_4$ spinel can be inhibited by the incorporation of Na$^+$ or K$^+$. This will be discussed in detail in Chapter 4.

3.4.3 Agglomeration and attrition

Agglomeration and attrition of the oxygen carriers are important aspects, considering that the CLOU process will be operated most likely in a fluidized beds configuration. In the CLOU experiments reported here, agglomeration was not observed regardless of the CuO content and the support material used. However, size analysis of Al$_2$O$_3$-stabilized oxygen carriers recovered after 25 CLOU cycles revealed a significant fraction of particles smaller than 300 µm. On the other hand, only a small amount of particles with d$_p$ < 300 µm were recovered when MgAl$_2$O$_4$-stabilized oxygen carriers (80 wt. % CuO) were used. These observations indicate that MgAl$_2$O$_4$-stabilized oxygen carriers containing 80 wt. % or less CuO are suitable oxygen carrier for the CLOU process.
3.5 Conclusions

This Chapter is concerned with the synthesis of CuO-rich, Al₂O₃- or MgAl₂O₄ stabilized oxygen carriers for the CLOU process. The oxygen carriers were calcined at two different temperatures, viz. 800 °C and 1000 °C. The results reported here show that the mechanical and structural properties of the oxygen carriers can be adjusted via the calcination temperature. Furthermore, it was observed that calcination at high temperatures shifted the onset temperature of CuO reduction (in N₂) to higher temperatures. Scanning electron micrographs of the oxygen carriers calcined at 1000 °C revealed a platelet-like morphology of CuO. Using MgAl₂O₄ as a support, the surface of the oxygen carriers was found to be uniformly covered with nanometer-sized MgAl₂O₄ grains. On the other hand, agglomerates of nanometer-sized CuAl₂O₄ grains could be identified on the surface of Al₂O₃-stabilized CuO. For Al₂O₃-stabilized oxygen carriers, the reduction of CuAl₂O₄ in N₂ was not fully reversible. As a consequence, the oxygen release capacity of Al₂O₃-stabilized oxygen carriers was significantly below its theoretical value. Based on thermogravimetric and XRD measurements, a reaction mechanism for Al₂O₃-stabilized CuO was proposed. The oxygen uncoupling capacity of MgAl₂O₄-stabilized oxygen carriers was stable and close to the theoretical values. MgAl₂O₄-stabilized CuO that contains 80 wt. % CuO was identified as a suitable material for the CLOU process owing to its stability, attrition and agglomeration resistance and high oxygen carrying capacity.
Chapter 4

Na⁺ doping to increase the oxygen uncoupling, reduction and charge transport characteristics of Al₂O₃-stabilized CuO

4.1 Introduction

The phase diagram of the Cu₂O-CuO-Al₂O₃ system shows that at temperatures > 600 °C, Al₂O₃ can form solid solutions with CuO, viz. the CuAl₂O₄ spinel or delafossite (CuAlO₂). As demonstrated in Chapter 2, the CuO present in the spinel phase is fully reducible under CLC conditions. Therefore, the formation of CuAl₂O₄ does not reduce the oxygen carrying capacity of Al₂O₃-stabilized CuO. However, the formation of CuAl₂O₄ does affect negatively the CLOU performance of Al₂O₃-stabilized CuO owing to the irreversible decomposition of CuAl₂O₄ to CuAlO₂ and the low oxygen equilibrium partial pressure of the CuAl₂O₄-CuAlO₂ couple (as shown in Chapter 3). Furthermore, the oxygen uncoupling capacity of the CuAl₂O₄-CuAlO₂ couple is comparatively low, viz. 0.044 g O₂/g CuAl₂O₄ that is less than half the value of the CuO-Cu₂O couple.

A strategy to avoid the reaction between Al₂O₃ and transition metal oxides is doping with small quantities of alkali metal ions (e.g. Li⁺, Na⁺ or K⁺). For example, Houalla et al. showed that Al₂O₃ and NiO did not form NiAl₂O₄ when doped with Li⁺. The inhibition of NiAl₂O₄ formation was explained by the preferential formation of an Al₂O₃-Li spinel. Using XRD and differential thermal analysis, El-Shobaky et al. studied the solid-solid reaction between CuO (16.3 wt. %) and Na⁺-doped Al₂O₃ in the temperature range 500–1000 °C. It was observed that the presence of Na⁺ prevented the reaction between CuO and Al₂O₃. This was attributed to the formation of a sodium aluminate phase at the surface of the Al₂O₃ grains. El-Shobaky et al. speculated that the sodium-aluminate phase limited the thermal diffusion of Cu²⁺ into the Al₂O₃ matrix, thus, preventing the formation of the copper
aluminate spinel. During the synthesis of Al$_2$O$_3$-stabilized CuO via co-precipitation, it was also observed that Na$^+$ that could not be removed by washing inhibited the formation of the spinel CuAl$_2$O$_4$ during the calcination step (see Chapter 2).

The effect of alkali metals on the cyclic redox performance of Al$_2$O$_3$-stabilized CuO-based oxygen carriers is currently unknown. Thus, in this Chapter the influence of Na$^+$ doping on the reduction, oxygen uncoupling and coke deposition characteristics of Al$_2$O$_3$-stabilized, CuO-based oxygen carriers was investigated. To achieve a homogeneous distribution of the dopant (Na$^+$), a sol-gel technique was utilized. The quantity of CuO in the oxygen carriers was fixed at 70 wt. %. The structure and reduction pathways of Na$^+$-doped, Al$_2$O$_3$-stabilized CuO were studied at 750 °C using X-ray absorption spectroscopy (XAS). In addition, the effect of Na$^+$ doping on charge transport was also assessed.

4.2 Experimental

4.2.1 Oxygen carrier synthesis

Na$^+$-doped (1, 3 or 5 wt. %), Al$_2$O$_3$-stabilized CuO (70 wt. % CuO) was synthesized using a sol-gel technique. In a typical synthesis, first an appropriate amount of aluminum isopropoxide ((C$_3$H$_7$O)$_3$Al) was added to deionized water. The obtained mixture was heated to 75°C and allowed to hydrolyze for 0.5 h under stirring. Subsequently, the solution was peptized with concentrated nitric acid. The molar ratio of Al$^{3+}$:H$_2$O:H$^+$ was 0.5:50:0.07. After peptization, condensation was allowed for 2 h at 90°C. Subsequently, an aqueous solution containing appropriate amounts of Cu(NO$_3$)$_2$·2.5H$_2$O and NaOH was added to the aluminum hydroxide gel. The mixture was heated under reflux for 12 h at 90°C and subsequently dried at 100°C. The final oxygen carrier was obtained by calcination in air in a muffle furnace at 900°C for 2 h (temperature ramp 5 °C/min). Throughout this Chapter, the abbreviation CuAlNax, where x is the wt. % of Na$^+$, will be used to refer to the different oxygen carriers synthesized.

4.2.2 Characterization techniques

A Bruker D8 Advance diffractometer, equipped with a Lynx eye super speed detector, was used to analyze the composition and crystallinity of (i) freshly calcined, (ii) reduced and (iii) cycled oxygen carriers. The diffractometer was operated at 40 mA and 40 kV using Cu K$_a$ radiation. Each sample was scanned in the range 2$\theta$ = 20–80°. The step size was 0.0275° and the scan time per step was 0.8 s. A scanning electron microscope (Zeiss LEO 1530 FEG)
was used to characterize the surface morphology of the freshly calcined oxygen carriers. A double-sided carbon tape was used to attach samples of the oxygen carrier onto an aluminum holder. Prior to imaging, the samples were sputter coated with an approximately 3 nm thick layer of platinum. The surface area and pore volume of the synthesized oxygen carriers were determined using a Quantachrome NOVA 4000e analyzer. Prior to the acquisition of the N\textsubscript{2} isotherms at -196 °C, each sample was degassed at 300 °C for approximately 3 h. The Brunauer et al.\textsuperscript{62} (BET) and the Barrett et al.\textsuperscript{63} (BJH) models were used to calculate, respectively, the surface area and the pore volume of the freshly calcined materials from the acquired isotherms.

The electrical conductivity and the activation energy for charge transport were determined by 4-point conductivity measurements.\textsuperscript{76-77} For the conductivity measurements, the materials were first crushed and then pelletized via uni-axial (40 kN for 2 min) and isostatic (1000 kN for 2 min) pressing. The pellets were sintered in air for 24 h at 1000 °C (the heating and cooling rate was 3 °C/min). The sintered pellets possessed a density of > 95% of the theoretical bulk density. Platinum electrodes were applied in a 4-point electrode arrangement on both sides of the pellets (Heraeus 3605). The resistance of each pellet was measured in air as a function of temperature (from 25 °C to 950 °C using a heating and cooling rate of 3 °C/min) by applying a DC voltage of 1 V (Keithley 2601B multimeter). To ensure reproducibility, three heating and cooling cycles were performed.

To determine the oxygen uncoupling characteristics and the CuO content of the synthesized oxygen carriers, N\textsubscript{2}-TPR experiments were performed in a TGA (Mettler Toledo TGA/DSC 1). In a typical experiment, ~15 mg of the oxygen carrier was heated from 25 °C to 1150 °C with a rate of 10 °C/min under a flow of N\textsubscript{2} (25 mL/min). Additionally, H\textsubscript{2}- and CH\textsubscript{4}-TPR experiments were performed to probe, respectively, the reduction characteristics and the propensity for coke formation of the synthesized oxygen carriers. In a typical experiment, ~15 mg of the oxygen carrier was heated from 25 °C to 1000 °C at a rate of 10 °C/min. At the end of the temperature ramp the material was kept at 1000 °C for an additional 30 min. H\textsubscript{2}- and CH\textsubscript{4}-TPR experiments were performed using 5 vol. % H\textsubscript{2} in N\textsubscript{2} and 10 vol. % CH\textsubscript{4} in N\textsubscript{2}, respectively. A Philips CM12 transmission electron microscope, operated at 100 kV, was used to image the carbon deposited.
4.2.3 Cyclic CLC and CLOU performance

The cyclic oxygen carrying capacity of the synthesized oxygen carriers was studied in a TGA at 900 °C. A mixture of 10 vol. % CH$_4$ in N$_2$ was used for CLC experiments and N$_2$ was used for CLOU experiments. The reduced materials were re-oxidized in air. In each reaction segment, the flow rate of the gases was 25 mL/min (25 ºC and 1 bar). In addition, a constant N$_2$ flow of 25 mL/min was used as purge flow over the microbalance. In a typical experiment, a small quantity (~25 mg) of the oxygen carrier was placed in an alumina pan and heated from room temperature to 900 ºC (10 ºC/min) in a flow of air. After reaching the reaction temperature, a reduction step was performed. The duration of the reduction steps during CLC and CLOU experiments was 390 s and 600 s, respectively. Subsequently, the oxygen carrier was re-oxidized in air. The oxygen carriers were re-oxidized for 390 s and 600 s for CLC and CLOU operation, respectively. In CLC experiments a N$_2$ flow was used to purge the reaction chamber for 60 s between each reduction and oxidation segment. The reduction and oxidation cycle was repeated 20 times.

4.2.4 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) was performed at the Swiss-Norwegian beamline (BM01B) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The measurements (Cu K-edge) were performed in transmission mode using a Si(111) double crystal monochromator. The energy was calibrated to the edge position of Cu foil (8979 eV). In order to study the local atomic order in the materials developed, extended X-ray absorption fine structure (EXAFS) data were collected (pellets using cellulose as a binder). In-situ X-ray absorption near edge structure (XANES) spectroscopy was performed to determine the reduction pathways of two representative oxygen carriers, viz. CuAlNa0 and CuAlNa5. A detailed description of the experimental set-up used for the XAS measurements is given in the Appendix A1.2. XAS data normalization and analysis were performed using the Athena and Artemis software packages (Demeter 0.9.20 software package). The structural parameters, such as interatomic distances, coordination number and the Debye-Waller factor, were obtained by nonlinear least-squares fitting of the acquired EXAFS data (k$^3$-weighted, k-range 3–13 Å$^{-1}$).
4.3 Results

4.3.1 Characterization of the calcined oxygen carriers

Figure 4.1. X-ray diffractograms of the calcined oxygen carriers. The following compounds were identified: (■) CuO, (♦) CuAl$_2$O$_4$ and (▲) NaAlO$_2$.

Figure 4.1 shows the X-ray diffractograms of the calcined oxygen carriers. CuAlNa0 and CuAlNa1 contained CuO and CuAl$_2$O$_4$, whereas CuAlNa3 and CuAlNa5 contained only CuO and NaAlO$_2$ (minor phase). The absence of CuAl$_2$O$_4$ in CuAlNa3 and CuAlNa5 is most likely due to Na$^+$ suppressing the formation of the spinel. Owing to the lack of diffraction peaks for Al$_2$O$_3$ in CuAlNa3 and CuAlNa5, Al$_2$O$_3$ is most likely present in an amorphous form. From Table 4.1 it can be seen that the average crystallite size of CuO in the synthesized oxygen carriers, estimated using the Scherrer equation, is ~23 nm (independent of the content of Na$^+$).

XANES and EXAFS spectroscopy were performed to gain a better insight into the local Cu environment. Figure 4.2(a) plots the Cu K-edge XANES spectra (acquired at room temperature) of the synthesized materials. For comparison, the Cu K-edge XANES spectra of pure, i.e. unsupported, CuO and CuAl$_2$O$_4$ are also shown in Figure 4.2(a). The edge energies (defined as the maximum in the first derivative of $\mu(E)$ with respect to energy) of CuO and CuAl$_2$O$_4$ were determined as 8983.3 eV and 8986.1 eV, respectively, in agreement with the literature. One of the features that clearly differentiates the XANES of CuO from that of
CuAl₂O₄ is a shoulder in the edge step (absent for CuAl₂O₄). From the inset 4.2(a1) of Figure 4.2(a) it can be seen that the shoulders in the edge step of CuAlNa0 and CuAlNa1 are less pronounced than for pure, *i.e.* unsupported CuO. This feature in the XANES of CuAlNa0 and CuAlNa1 can be attributed to the presence of a CuAl₂O₄ phase in these materials (as confirmed by XRD, Figure 4.1). On the other hand, except for a minor reduction in the intensity of the white line (inset 4.2(a2)), the XANES spectra of CuAlNa3 and CuAlNa5 resemble very well the reference spectra of CuO. Linear combination fitting (LCF) of the XANES data (weight fractions of CuO and CuAl₂O₄ on an Al₂O₃ free basis, Table 4.1) shows that the quantity of CuAl₂O₄ in the materials decreases with increasing Na⁺ content.

**Table 4.1.** Average crystallite size and the weight fraction of CuO and CuAl₂O₄ (Al₂O₃-free basis) in the calcined oxygen carriers. The average crystallite sizes were calculated from the (200) and (311) reflections of CuO and CuAl₂O₄, respectively. The weight fractions of the Cu²⁺-containing phases were determined from the XANES spectra using LCF.

<table>
<thead>
<tr>
<th>Material</th>
<th>CuO [nm]</th>
<th>CuAl₂O₄ [nm]</th>
<th>CuO [-]</th>
<th>CuAl₂O₄ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlNa0</td>
<td>23</td>
<td>38</td>
<td>0.71 ± 0.03</td>
<td>0.29 ± 0.03</td>
</tr>
<tr>
<td>CuAlNa1</td>
<td>21</td>
<td>34</td>
<td>0.75 ± 0.03</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>CuAlNa3</td>
<td>24</td>
<td>-</td>
<td>0.91 ± 0.03</td>
<td>0.09 ± 0.03</td>
</tr>
<tr>
<td>CuAlNa5</td>
<td>25</td>
<td>-</td>
<td>0.98 ± 0.02</td>
<td>0.02 ± 0.02</td>
</tr>
</tbody>
</table>

The experimentally determined *k*³-weighted EXAFS functions of the synthesized oxygen carriers as well as the references CuO and CuAl₂O₄ are given in Figure 4.2(b). The EXAFS functions of CuAlNa0, CuAlNa1 and CuAlNa3 show a reduction of the amplitude of the oscillations when compared to the CuO reference (*e.g.* see inset 4.2(b1)). Moreover, the EXAFS spectra of CuAlNa0, CuAlNa1 and CuAlNa3 contain features that can be ascribed to CuAl₂O₄ (*e.g.* see inset 4.2(b2)). These observations indicate that the (volume averaged) local environment of Cu in CuAlNa0, CuAlNa1 and CuAlNa3 is, due to the presence of CuAl₂O₄, different from pure CuO (in agreement with XRD and LCF analysis). On the other hand, the EXAFS data show that only CuAlNa5 has a similar signature as the CuO reference, indicating that 5 wt. % Na⁺ prevented the reaction between CuO and Al₂O₃.
Figure 4.2. Room temperature (a) XANES and (b) EXAFS spectra ($k^2$-weighted) of calcined (→) CuAlNa0, (→) CuAlNa1, (→) CuAlNa3, (→) CuAlNa5, (→) CuO and (→) CuAl$_2$O$_4$ measured at the Cu K-edge.
Figure 4.3. High resolution scanning electron micrographs of the oxygen carriers synthesized: (a) CuAlNa0, (b) CuAlNa1, (c) CuAlNa3 and (d) CuAlNa5.

Table 4.2. BET surface area and BJH pore volume of the freshly calcined oxygen carriers.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area [m²/g]</th>
<th>BJH pore volume [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlNa0</td>
<td>14</td>
<td>0.05</td>
</tr>
<tr>
<td>CuAlNa1</td>
<td>20</td>
<td>0.06</td>
</tr>
<tr>
<td>CuAlNa3</td>
<td>12</td>
<td>0.04</td>
</tr>
<tr>
<td>CuAlNa5</td>
<td>10</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Scanning electron micrographs of the synthesized oxygen carriers are given in Figure 4.3. The oxygen carriers CuAlNa0 and CuAlNa1 reveal a porous surface morphology (in line with their comparatively high surface area as determined by N₂ adsorption, Table 4.2). Increasing the Na⁺ content to 5 wt. % led to a densification of the material. The different morphology of CuAlNa3 and CuAlNa5 was accompanied by a decrease in surface area.
4.3.2 Temperature programmed reduction

![Temperature programmed reduction graph]

**Figure 4.4.** $\text{N}_2$-TPR profiles of the synthesized oxygen carriers: (—) CuAlNa0, (—) CuAlNa1, (—) CuAlNa3 and (—) CuAlNa5.

<table>
<thead>
<tr>
<th>Material</th>
<th>CuAlNa0</th>
<th>CuAlNa1</th>
<th>CuAlNa3</th>
<th>CuAlNa5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO content [wt. %]</td>
<td>70.4</td>
<td>69.9</td>
<td>71.1</td>
<td>70.9</td>
</tr>
</tbody>
</table>

To determine the influence of $\text{Na}^+$ on the oxygen uncoupling characteristics of the synthesized oxygen carriers, $\text{N}_2$-TPR experiments were performed in a TGA. Figure 4.4 plots the normalized weight loss as a function of temperature for the materials synthesized. It was observed that the reduction of all oxygen carriers (defined as the temperature at which the oxygen carrier has lost 2 % of the total weight loss) starts at ~770 °C, independent of the $\text{Na}^+$ loading. As expected, the reduction of CuAlNa0, CuAlNa1 and CuAlNa3 occurred in two steps. In the first step (temperature range 750–890 °C), CuO is reduced to Cu$_2$O via:

$$4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2 \quad (4.1)$$

The comparatively slow reduction of CuAl$_2$O$_4$ to CuAlO$_2$ occurred in the second step (temperature range 890–1050 °C), according to:

$$4\text{CuAl}_2\text{O}_4 \rightarrow 4\text{CuAlO}_2 + 2\text{Al}_2\text{O}_3 + \text{O}_2 \quad (4.2)$$
Figure 4.5. (a) H₂- and (b) CH₄-TPR profiles of the synthesized oxygen carriers: (—) CuAlNa0, (—) CuAlNa1, (—) CuAlNa3 and (—) CuAlNa5.

The (apparent) rate of CuAl₂O₄ reduction was slower for CuAlNa1 when compared to CuAlNa0. Currently the slower reduction kinetics of CuAl₂O₄ in CuAlNa1 cannot be explained unequivocally. XRD analysis of the reduced CuAlNa0, CuAlNa1 and CuAlNa3 confirmed the presence of Cu₂O, CuAlO₂ and Al₂O₃. Due to the absence of CuAl₂O₄, the reduction of CuAlNa5 occurred in a single step. The X-ray diffractogram of reduced CuAlNa5 shows peaks due to Cu₂O and NaAlO₂ only. The CuO content in the synthesized
oxygen carriers, as determined from N₂-TPR experiments, was close to the theoretically expected value of 70 wt. %, see Table 4.3.

H₂-TPR experiments, Figure 4.5(a), were performed to study the effect of Na⁺ on the reduction characteristics of the synthesized materials. The peak positions of the H₂-TPR profiles are summarized in the inset of Figure 4.5(a). For CuAlNa0 and CuAlNa1, the reduction started at ~245 °C, with peaks located at ~310 °C and ~322 °C, respectively. A second peak was located at ~415 °C and ~385 °C for, respectively, CuAlNa0 and CuAlNa1. The first peak can be assigned to the reduction of CuO to Cu, whereas the second peak corresponds to the reduction of CuAl₂O₄ to Cu and Al₂O₃. For CuAlNa3 and CuAlNa5, reduction started at ~280 °C with peaks located at ~332 °C and ~335 °C, respectively. Interestingly, a reduction peak for CuAl₂O₄ was not observed in the H₂-TPR profiles of CuAlNa3, probably due to a very small quantity of CuAl₂O₄ in CuAlNa3 (see Table 4.1). Overall, it was observed that increasing Na⁺ loadings led to increasing reduction temperatures. X-ray diffractograms of the reduced materials confirmed the presence of Cu in the reduced oxygen carriers. In the case of CuAlNa5, also NaAlO₂ was identified in the reduced materials (minor phase).

The reduction and carbon deposition characteristics of the synthesized oxygen carriers were assessed further using CH₄-TPR. The CH₄-TPR profiles of the synthesized oxygen carriers are plotted in Figure 4.5(b). The reduction of CuAlNa0 started at ~530 °C and was completed at ~710 °C. In contrast to the N₂- and H₂-TPR measurements, a separate reduction step for CuAl₂O₄ was not observed in the CH₄-TPR measurements. This would indicate that using CH₄, CuO and CuAl₂O₄ are reduced simultaneously or there is a significant overlap between the reduction of CuO and CuAl₂O₄, giving in turn, an apparent single step reduction. The reduction of Na⁺-doped oxygen carriers started at ~560 °C irrespective of the Na⁺ content, i.e. at a higher temperature (+30 °C) compared to the un-doped material. For CuAlNa0, a substantial increase in weight was observed for temperatures > 750 °C. This is due to the deposition of coke via the CH₄ decomposition reaction, viz.:

\[ CH₄ \rightarrow C + H₂ \]  

(4.3)

On the other hand, CuAlNa1 revealed a comparatively low propensity to coke formation and, compared to CuAlNa0, the onset of carbon deposition was shifted to higher temperatures. Transmission electron microscopy (Figure 4.6) revealed that the carbon deposited on CuAlNa0 and CuAlNa1 was in the form of filaments and whiskers. Importantly,
no carbon deposition was observed in the transmission electron micrographs of CuAlNa3 and CuAlNa5; a very favorable characteristic for CLC. The increased resistance of Na⁺-doped oxygen carriers to carbon formation can be attributed to the ability of alkali metals to stabilize preferably CHₓ⁻⁻ species instead of C⁻⁻ surface intermediates. The X-ray diffractograms of the CH₄-reduced oxygen carriers showed peaks due to Cu. For CuAlNa5, Bragg reflections due to NaAlO₂ were also identified.

![Image](image_url)

**Figure 4.6.** Transmission electron micrographs of (a) CuAlNa0 and (b) CuAlNa1 after CH₄-TPR.

### 4.3.3 CLC and CLOU performance

The cyclic CLOU and CLC performance of the synthesized oxygen carriers was evaluated in a TGA at 900 °C. The normalized oxygen carrying capacity ($R_n$) defined as

$R_n = \frac{\text{measured weight loss}}{\text{theoretical weight loss}}$  \hspace{1cm} (4.4)

is plotted in Figures 4.7(a) (CLOU) and (b) (CLC) as a function of cycle number. As expected, under CLOU conditions the normalized oxygen carrying capacity of CuAlNa0 and CuAlNa1 decreased with cycle number. This behavior is due to the slow oxidation kinetics of CuAlO₂ back to CuAl₂O₄. Over the 20 cycles tested, an approximately 16 % decrease in the oxygen carrying capacity was observed for CuAlNa0 and CuAlNa1. Doping the oxygen carrier with 1 wt. % Na⁺ did not prevent the formation of a solid solution
between CuO and Al₂O₃ (as confirmed by XRD and XAS). Thus, the CLOU performances of CuAlNa₀ and CuAlNa₁ are very similar. In the X-ray diffractogram of cycled (oxidized state) CuAlNa₀ and CuAlNa₁, CuO, CuAlO₂ and Al₂O₃ were identified. On the other hand, for CuAlNa₃ and CuAlNa₅ the oxygen carrying capacity was only reduced by ~3 % over the first four cycles. From the fifth cycle onwards, the oxygen carrying capacity of CuAlNa₃ remained stable, reaching 97 % of the theoretically predicted oxygen carrying capacity of the material. The X-ray diffractogram of cycled CuAlNa₃ showed weak peaks due to CuAl₂O₄ along with CuO and NaAlO₂. This confirms (in line with XAS data) that doping CuO-Al₂O₃ with 3 wt. % Na⁺ is not sufficient to completely avoid the formation of a solid solution between CuO and Al₂O₃. In the case of CuAlNa₅, in the ninth cycle the normalized oxygen carrying capacity reached 100 % of the theoretically predicted oxygen carrying capacity and remained stable for the subsequent cycles. This implies a fully reversible reduction-oxidation of the CuO-Cu₂O couple. The X-ray diffractogram of cycled (oxidized state) CuAlNa₅ showed peaks due to CuO and NaAlO₂ only, i.e. the spinel CuAl₂O₄ is not present in CuAlNa₅. The slight drop in the oxygen carrying capacity during the first five cycles is probably due to some small changes in the kinetics of the oxidation reaction over the initial CLOU cycles, as shown in Figure 4.8.
Figure 4.7. Normalized oxygen carrying capacity of the oxygen carriers synthesized, as determined in a TGA at 900 °C under (a) CLOU and (b) CLC conditions: (♦) CuAlNa0, (■) CuAlNa1, (▲) CuAlNa3 and (●) CuAlNa5.
Turning to the CLC performance of the synthesized oxygen carriers, a gradual decrease in the normalized oxygen carrying capacity was observed for CuAlNa0 (Figure 4.7(b)). On the other hand, all Na⁺-doped oxygen carriers showed stable oxygen carrying capacities close to 1 over the 20 redox cycles tested. The X-ray diffractograms of cycled (oxidized state) CuAlNa0 and CuAlNa1 showed reflections due to CuO and CuAl₂O₄. On the other hand, the XRD data of CuAlNa3 and CuAlNa5 showed only peaks due to CuO and NaAlO₂. As shown previously (Chapter 2) CuAl₂O₄ is fully reducible under CLC conditions and does not reduce the oxygen carrying capacity of CuAlNa0. The temporally resolved mass loss profiles of CuAlNa0 (Figure 4.9(a)) revealed that the rate of oxidation of CuAlNa0 decreased with cycle number, leading in turn to a decreasing oxygen carrying capacity with cycle number (the oxidation time was fixed to 390 s). In contrast, all Na⁺ doped oxygen carriers possessed not only higher oxidation rates (compared to the un-doped material), but also maintained their high oxidation rates over the 20 cycles tested (Figure 4.9(b)). Therefore, even CuAlNa1, despite containing CuAl₂O₄, showed a stable cyclic oxygen carrying capacity under CLC conditions.
Figure 4.9. Fractional conversion as a function of cycle number during re-oxidation of (a) CuAlNa0 and (b) CuAlNa5 under CLC conditions at 900 °C: (—) first cycle, (—) fifth cycle, (—) tenth cycle, (—) fifteenth cycle and (—) twentieth cycle.

The long term redox stability of CuAlNa5 was evaluated further in a TGA at 900 °C for 100 CLC and CLOU cycles. Figure 4.10 plots the normalized oxygen carrying capacity of CuAlNa5 under both CLC and CLOU conditions as a function of cycle number. Under both CLC and CLOU conditions CuAlNa5 showed stable oxygen carrying capacities close to one over the 100 redox cycles tested, indicating that there was no sodium leaching at the high
operating temperatures. Even after 100 cycle, CuAl₂O₄ or CuAlO₂ were not observed in the X-ray diffractograms (Figure 4.11) of cycled (oxidized state) CuAlNa₅, confirming further the long term stability of Na⁺-doped and Al₂O₃-stabilized CuO.

**Figure 4.10.** Normalized oxygen carrying capacity of CuAlNa₅, as determined in a TGA at 900 °C under (□) CLC and (□) CLOU conditions.
Figure 4.11. X-ray diffractograms of CuAlNa5 (100 cycles, oxidized form): (a) CLC and (b) CLOU conditions at 900 °C. The following compounds were identified: (■) CuO and (▲) NaAlO₂.

4.3.4 In-situ XANES spectroscopy

In-situ XANES spectroscopy was performed to investigate the reduction pathways of un-doped and Na⁺-doped (5 wt. %), Al₂O₃-stabilized CuO at 750 °C. In total three redox cycles were performed for each material. Figures 4.12(a) and (b) show the temporal changes in the Cu K-edge XANES spectra of, respectively, CuAlNa0 and CuAlNa5 (first reduction step using 5 vol. % H₂ in He). Each spectrum plotted was acquired in He after a 5 s pulse of the reducing gas was released into the bed. Figure 4.12 reveals that at 750 °C the reduction of the oxygen carriers commenced with the first H₂ pulse, i.e. an induction period was not observed. The absence of an induction period at 750 °C is most likely due to the high thermal disorder in the materials as confirmed by the EXAFS spectra of CuAlNa0 and CuAlNa5 (Figure 4.13).
Figure 4.12. Time-resolved (5 s) Cu K-edge XANES spectra during reduction (5 vol. % H$_2$ in He) of (a) CuAlNa0 and (b) CuAlNa5 at 750 °C. The red (−) and blue (—) lines correspond to the initial and final states, respectively.
Figure 4.13. Fourier transformed EXAFS functions ($k^2$-weighted) of (a) CuAlNa0 and (b) CuAlNa5 measured at the Cu K-edge: (—) 25 °C and (—) 750 °C.

The significant reduction of the amplitude of the Fourier transformed EXAFS functions recorded at 750 °C when compared to data acquired at room temperature is due to an increase in thermally-induced disorder. Rodriguez et al. argued that the occurrence of an induction period is related to the formation of defect sites on the metal oxide surface. These active sites have a high activity for the dissociation of H$_2$, but have, however, only been observed at low temperatures, i.e. $T < 310 \, ^\circ$C. For example, the in-situ XAS

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measurements of Kim et al. showed an induction period in the temperature range 250–300 °C (5 vol. % H\textsubscript{2} in He with a flow rate > 15 mL/min; commercial, pure CuO powder). Kim et al. also reported that the duration of the induction period decreased with increasing temperature.

![Figure 4.14](image)

**Figure 4.14.** Weight fractions of (–□–) CuO, (–○–) CuAl\textsubscript{2}O\textsubscript{4}, (–◊–) Cu\textsubscript{2}O and (–Δ–) Cu during the reduction of (a) CuAlNa0 and (b) CuAlNa5 calculated using linear combination fitting of the acquired Cu K-edge XANES data. The reduction was performed at 750 °C using 5 s pulses of 5 vol. % H\textsubscript{2} and 95 vol. % He. 30 H\textsubscript{2} pulses were used in total.

The reduction pathways of CuAlNa0 and CuAlNa5 (Figures 4.14(a) and (b), respectively) were determined using LCF of the acquired XANES data. Figure 4.14 confirms that the reduction of both oxygen carriers proceeds *via* the Cu\textsubscript{2}O intermediate. The transition though the Cu\textsubscript{2}O intermediate during reduction was supported further by principal component analysis (PCA). PCA of the recorded XANES data of CuAlNa0 and CuAlNa5 confirmed that all spectra could be reconstructed when using the four reference compounds, *viz.* CuO, CuAl\textsubscript{2}O\textsubscript{4}, Cu\textsubscript{2}O and Cu. Using DFT, Kim *et al.* showed that under reducing conditions CuO can reach metastable states that possess a large number of oxygen vacancies. A transition from these metastable states to Cu\textsubscript{2}O is associated with large variations in the cell parameters.
of CuO, whereas a very small amount of energy (total energy of unit cell calculated using DFT) is released during the transition from metastable CuO (CuO with large number of oxygen vacancies) to Cu$_2$O. Consequently, Kim et al.\cite{Kim2015} proposed that Cu$_2$O intermediates are only formed for slow reduction rates. On the other hand, under fast oxygen removal conditions the following transitions: CuO $\rightarrow$ metastable CuO $\rightarrow$ Cu are favored energetically. It can be speculated that in the present work the use of H$_2$ pulses (simulating a slow reduction) allowed the formation of the Cu$_2$O intermediate during reduction. Within the temporal resolution of the XAS spectrometer, the formation of the Cu$_2$O intermediate was not observed when a continuous flow of 25 mL/min of 5 vol. % H$_2$ in He was used for reduction (simulating a fast reduction).

The in-situ XAS results plotted in Figure 4.14(a) also show that in the first reduction segment of CuAlNa0, CuO and CuAl$_2$O$_4$ were reduced simultaneously to Cu$_2$O. The reduction of CuO and CuAl$_2$O$_4$ to Cu$_2$O was completed within the first 60 s. The further reduction of Cu$_2$O to Cu started after 20 s. At the end of the reduction step (150 s), the material still contained ~15 wt. % Cu$_2$O, indicative of a comparatively slow reduction rate for Cu$_2$O. Nonetheless, XANES confirmed that CuO, which is in a solid solution with Al$_2$O$_3$, is fully reducible to Cu via the Cu$_2$O intermediate. Thus, the formation of CuAl$_2$O$_4$ does not reduce the oxygen carrying capacity of the synthesized oxygen carriers. The composition of CuAlNa0 at the end of the first redox cycle (i.e. after re-oxidation with 5 vol. % O$_2$ in He) was 62.5 wt. % CuO, 21.0 wt. % Cu$_2$O and 16.5 wt. % CuAl$_2$O$_4$. The incomplete oxidation of Cu$_2$O to CuO during the fixed oxidation time (575 s) is due to the sluggish oxidation kinetics of the Cu$^+$-Cu$^{2+}$ transition.\cite{Kim2015} In the reduction step of the second and third redox cycle, the reduction of CuO and CuAl$_2$O$_4$ was completed within 20 second, i.e. three times faster when compared to the first cycle. Similarly, the (apparent) rate of reduction of Cu$_2$O also increased slightly with cycle number. As a consequence, Cu$_2$O was fully reduced to Cu in the third cycle.
For CuAlNa5, only CuO was identified in the fresh and re-oxidized materials. In the first 15 s of the reduction segment of the first cycle, CuO was reduced primarily to Cu$_2$O; only a minor quantity of Cu was detected. After 15 s, the fraction of Cu started to increase gradually. The reduction of CuO and Cu$_2$O was completed within 45 s and 90 s, respectively. Here, the apparent rate of reduction of CuO and Cu$_2$O was again found to increase with cycle number. For example, in the second and third cycle, Cu occurred already after the first H$_2$ pulse (5 s). Furthermore, it was observed that for CuAlNa5 the quantity of Cu$_2$O formed during reduction decreases with increasing cycle number. From Figure 4.14(a) and (b) it is evident that the reduction kinetics of CuAlNa5 is faster compared to CuAlNa0. The influence of Na$^+$ on the reduction pathways and kinetics will be discussed in detail further below. To explain the increase in the reduction kinetics with cycle number, room temperature EXAFS data of fresh and cycled CuAlNa5 were recorded. Compared to fresh CuAlNa5, the Fourier transformed EXAFS function of cycled (oxidized) CuAlNa5 shows an appreciably reduced height of the peaks corresponding to the first and second coordination spheres (Figure 4.15). Fitting of the first shell of cycled CuAlNa5 shows an increase in the Debye-Waller factor and a decrease in the Cu-O coordination number compared to fresh CuAlNa5 (Table 4.4), indicative of an increasing defect structure in CuO with cycle number.

**Figure 4.15.** Fourier transformed EXAFS functions ($k^2$-weighted) of (—) fresh and (—) cycled CuAlNa5 measured at the Cu K-edge at 25 ºC.
Table 4.4. Structural parameters of the first (Cu-O) shell of fresh and cycled CuAlNa5, as determined by refinement of the theoretical CuO structure.

<table>
<thead>
<tr>
<th>Material</th>
<th>N</th>
<th>R</th>
<th>$\sigma^2$</th>
<th>$k$-range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlNa5 (fresh)</td>
<td>3.60 ± 0.38</td>
<td>1.94 ± 0.01</td>
<td>0.0038 ± 0.0013</td>
<td>3.0–12.0</td>
</tr>
<tr>
<td>CuAlNa5 (cycled)</td>
<td>3.03 ± 0.39</td>
<td>1.93 ± 0.01</td>
<td>0.0040 ± 0.0016</td>
<td></td>
</tr>
</tbody>
</table>

$N$ = coordination number; $R$ = distance; $\sigma^2$ = EXAFS Debye-Waller factor

4.3.5 Conductivity measurements

Based on DFT calculations, Li et al.\cite{89, 90} argued that the redox performance of transition metal oxides depends critically on the activation energy for the countercurrent conduction of ions and electrons through the oxygen carrier. However, there is currently very little experimental evidence available to support this modelling result. In order to investigate the influence of Na$^+$ doping on the activation energy for charge transport, 4-point electrical conductivity measurements were performed. In Figure 4.16(a) the measured resistivity of CuAlNa0 and CuAlNa5 is plotted as a function of temperature. CuAlNa5 has a lower resistivity than CuAlNa0 and the resistivity decreases with increasing temperature. The resistivity data were further analyzed by fitting the following Arrhenius relationship:

$$\sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)$$  \hspace{1cm} (4.5)

where $\sigma_0$, $E_a$ and $k$ are, respectively, a proportionality constant, the activation energy for charge conduction and the Boltzmann constant. Plotting $\ln(\sigma T)$ as a function of $1/T$ yielded two distinct regions. Thus, the low and high temperature regimes were fitted by separate activation energies. For temperatures < 600 ºC, the activation energy for charge transport in CuAlNa0 and CuAlNa5 was determined as 0.152 eV and 0.098 eV, respectively (see Figure 4.16(b)). At ~600 ºC, an increase in activation energy is observed, indicative of a change in the charge transport mechanism. For temperatures exceeding 600 ºC, an activation energy of 0.448 and 0.405 eV was determined for CuAlNa0 and CuAlNa5, respectively.
It is worth noting here that CuO is a p-type semiconductor.\textsuperscript{91, 92} Jeong and Choi\textsuperscript{93} showed that conduction at low temperatures is due to the hopping of charge carriers in metal deficient CuO, \emph{i.e.} Cu\textsubscript{1-\(y\)}O. Using 4-point conductivity measurements, Jeong and Choi\textsuperscript{93} determined the activation energy for charge carrier hopping as 0.1 ± 0.01 eV, which is in good agreement with the values obtained here (for \(T < 600^\circ\text{C}\)). The high temperature region gives the intrinsic conductivity of the material. In the literature the activation energy for
charge transport through unsupported CuO at high temperatures (for $T > 600$ °C) was determined as $0.7 \pm 0.04$ eV.\textsuperscript{93} This value is slightly higher than the one obtained through this work. The difference can most likely be attributed to morphological difference between commercial CuO and the material synthesized here.\textsuperscript{93}

### 4.4. Discussion

#### 4.4.1 Effect of Na\textsuperscript{+} on the morphological properties of Al\textsubscript{2}O\textsubscript{3}-stabilized CuO

It was observed that the average crystallite size of CuO in the synthesized oxygen carriers is not affected by Na\textsuperscript{+} doping (Table 4.1). This implies that Na\textsuperscript{+} doping has no pronounced solute drag or strain effect on the crystallite size development of CuO.\textsuperscript{94, 95} On the other hand, Na\textsuperscript{+} doping significantly modifies the surface morphology of the oxygen carriers synthesized (Figure 4.3). Based on visual inspection of the electron micrographs, the sintering tendency of the grains was found to increase with increasing Na\textsuperscript{+} content. It has been reported that the addition of alkali metals cations to metal oxides, e.g. Li\textsuperscript{+} to ceria, can increase sintering through an increased atomic mobility at the grain boundaries.\textsuperscript{96}

#### 4.4.2 Influence of Na\textsuperscript{+} on reduction kinetics and charge transport characteristics

From in-situ XANES spectroscopy results (Figure 4.14) it is evident that the (apparent) rate of reduction of CuAlNa\textsubscript{5} is appreciably faster when compared to CuAlNa\textsubscript{0}, albeit the same reduction pathway was followed, viz. CuO $\rightarrow$ Cu\textsubscript{2}O $\rightarrow$ Cu. As the oxygen carrier CuAlNa\textsubscript{5} has a smaller surface area than CuAlNa\textsubscript{0} (Table 4.2), the faster reduction kinetics of CuAlNa\textsubscript{5} cannot be explained by surface area effects. Thus, the fast reduction kinetics of CuAlNa\textsubscript{5} can be attributed to Na\textsuperscript{+}-induced defect structures. Owing to differences in the oxidation states and ionic radii of Cu ions (0.73 Å) and Na ions (1.02 Å), doping Al\textsubscript{2}O\textsubscript{3}-stabilized CuO with Na\textsuperscript{+} creates aliovalent substitution defects in the oxygen carrier.\textsuperscript{97, 98} Aliovalent substitution defects lower the positive charge within the oxygen carrier, therefore oxygen vacancies or holes are generated as a charge compensation mechanism to maintain the overall charge neutrality. These oxygen vacancies or holes facilitate the transport of oxygen (O\textsuperscript{2-}) and electronic carriers during redox reactions. Comparing the electrical
transport characteristics of Na+-doped CuO (CuAlNa5) and un-doped CuO (CuAlNa0), it is clear that Na+ doping increases the reduction kinetics of CuO by (i) lowering the activation energy for charge transport by ~0.05 eV and (ii) increasing the overall conductivity by a factor of 2. The lowering of the activation energy for charge transport can be ascribed to Na+-induced modifications in the electronic structure of CuO in line with XANES data and the absence of a spinel phase in CuAlNa5.

4.4.3 Influence of cycle number on the reduction kinetics

Figure 4.14 shows that the reduction kinetics of both CuAlNa0 and CuAlNa5 increase with cycle number. This observation is consistent with the TGA and fluidized bed measurements reported in, respectively, Chapter 2 and 3, viz. an increasing reduction rate of Al2O3-stabilized CuO with cycle number. The Fourier transformed EXAFS functions of fresh and cycled CuAlNa5 (Figure 4.15 and Table 4.4) revealed that the number of defects (e.g. oxygen vacancies) in the CuO structure increases with number of repeated redox cycles resulting in an increasing distortion of the local atomic order. It is likely that the increasing structural disorder of CuO with cycle number facilitates the transport of oxygen ions and electrons during reduction, which in turn leads to faster reduction kinetics.

4.4.4 Relation between reduction kinetics and pathways

The quantity of Cu2O formed during the reduction of CuAlNa5 was found to decrease with increasing cycle number (in-situ XAS measurements, Figure 4.14(b)). The decreasing quantity of Cu2O with cycle number suggests a change in the reduction pathway from a sequential (CuO → Cu2O → Cu) to a direct transition (CuO → Cu). Indeed, it is conceivable that the increasing (apparent) reduction kinetics with cycle number, as discussed above, is a direct consequence of this change in reduction pathway with cycle number. This observation is an agreement with the report of Kim at al.87 showing that the reduction kinetics of pure CuO plays an important role in the reduction pathway. The sequential reduction of CuO occurs only under slow oxygen removal conditions. Therefore, an increasing rate of reduction with cycle number (as observed here) would favor the CuO → Cu transition and change the reduction pathway from sequential to direct. The change of the reduction pathway of CuO would have important consequences for the oxidation mechanism of gaseous hydrocarbons. In the case of a sequential reduction pathway the reaction between CH4 and CuO proceeds with both the lattice oxygen of CuO and
molecular oxygen released via the CuO → Cu₂O transition. For the direct reduction of CuO, only lattice oxygen will be available for the oxidation of CH₄.

### 4.5 Conclusions

In this Chapter, the effect of Na⁺ doping on the local structure, electronic properties and cyclic redox characteristics of Al₂O₃-stabilized CuO is probed and characterized in detail. Using a combination of XAS, XRD and conductivity measurements it was demonstrated that the improved redox performance of Na⁺-doped oxygen carriers under CLC conditions is due to Na⁺-induced changes in the electronic structure of CuO and the suppression of the formation of a spinel phase. These structural changes led to enhanced electronic transport kinetics possibly due to the generation of oxygen vacancies compensating the lower charge of Na⁺ when compared to Cu²⁺. The absence of the CuAl₂O₄ phase led to a high redox stability under CLOU conditions. Utilizing in-situ XANES spectroscopy, it was shown that the reduction of both un-doped and doped CuO proceeds via the Cu₂O intermediate. The (apparent) rate of reduction increased with cycle number owing to an increasing structural disorder. As a consequence, with cycle number the reduction pathway changed from sequential (CuO → Cu₂O → Cu) to a direct CuO → Cu transition.
Chapter 5

Development of a highly efficient oxygen storage material with intrinsic coke resistance: CuO-CeO$_{2-x}$

5.1 Introduction

Owing to its low tendency to form solid solutions with transition metal oxides, ceria has a high potential as a support material for chemical looping. In addition, ceria can also contribute to the storage and release of oxygen via a non-stoichiometric redox reaction. Furthermore, CeO$_{2-x}$ is a mixed ionic-electronic conducting material in which the oxygen non-stoichiometry is balanced by a mixture of Ce$^{4+}$ and Ce$^{3+}$ oxidation states.$^{99, 100}$ Ceria has a simple cubic structure,$^{101}$ possesses a high Tammann temperature (1064 °C)$^{102, 103}$ and shows no solid solution formation in the CuO-CeO$_{2-x}$ system.$^{104, 105}$ Very recently, Hedayati et al.$^{103}$ reported promising redox characteristics of CuO-based, ceria or gadolinium oxide-doped ceria supported oxygen carriers. Using thermogravimetric analysis, Wang et al.$^{106}$ measured the O/metal atom ratio of ceria for oxygen partial pressures in the range $10^{-5}$–$10^{-20}$ bar at 1000 °C. At a fixed oxygen partial pressure, Wang et al.$^{106}$ demonstrated that the doping of ceria (e.g. using Gd) reduces the O/metal atom ratio of ceria. This decrease in the O/metal atom ratio has potential implications for chemical looping applications, since the uptake and release of oxygen in Gd-doped CeO$_{2-x}$ is strongly reduced compared to CeO$_{2-x}$.

In this Chapter, the potential of CeO$_{2-x}$-supported CuO as an oxygen carrier for CLC and CLOU is determined. The cyclic redox stability (using CH$_4$ as a fuel) and oxygen release capacity are investigated in detail and discussed in the light of the material’s microstructure and phase characteristics. The oxygen carriers were synthesized using a co-precipitation technique and contained up to 60 wt. % CuO. The performance of CeO$_{2-x}$-supported CuO was compared to Al$_2$O$_3$-supported CuO.
5.2 Experimental

5.2.1 Oxygen carrier synthesis

CeO\textsubscript{2-x}-supported, CuO-based oxygen carriers containing 50 or 60 wt. % CuO were prepared using a co-precipitation technique. In a typical synthesis, appropriate amounts of Cu(NO\textsubscript{3})\textsubscript{2}·2.5H\textsubscript{2}O and Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O were dissolved in 100 mL of deionized water (15 MΩ·cm at 25 °C). Subsequently, a 2 M NaOH solution was fed dropwise to the nitrate solution under magnetic stirring until a pH value of 10.0 was reached. The resulting precipitate was aged for 150 min at room temperature and subsequently washed several times with deionized water to remove excess Na\textsuperscript{+} and nitrate ions. Once the electrical conductivity of the filtrate was ~150 μS/cm, the cake of the 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. Finally, the calcined oxygen carrier was crushed and sieved into the size ranges 53–106 μm and 300–425 μm. For comparison, Al\textsubscript{2}O\textsubscript{3}-supported CuO containing 50 wt. % CuO was synthesized using a similar protocol (co-precipitation was performed at pH 8.5 and Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O was used as the aluminum precursor). Throughout this Chapter, the following nomenclature will be used to describe the oxygen carriers: the symbol Cu is followed by the weight percentage of CuO and an abbreviation for the support (i.e. Ce or Al). For example, Cu60Ce is a CeO\textsubscript{2-x}-stabilized oxygen carrier that contains 60 wt. % CuO.

5.2.2 Oxygen carrier characterization

The composition of the calcined, reduced and cycled oxygen carriers was determined using XRD (Bruker D8 Advance). The diffractometer was mounted with a Lynx eye super speed detector and operated at 40 kV and 40 mA using Cu K\textsubscript{α} radiation. The X-ray diffractograms were acquired within the range of 2θ = 20–80° with a step size of 0.0275° per second. The average crystallite sizes of CuO, CeO\textsubscript{2-x} and CuAl\textsubscript{2}O\textsubscript{4} were estimated using Scherrer’s equation.\textsuperscript{72} N\textsubscript{2}-physisorption isotherms of the freshly calcined and cycled oxygen carriers were acquired at -196 °C using a Quantachrome NOVA 4000e analyzer. Prior to the acquisition of the isotherms, the oxygen carriers were degassed at 300 °C for at least 2 h. The Brunauer-Emmett-Teller (BET)\textsuperscript{62} and Barrett-Joyner-Halenda (BJH)\textsuperscript{63} models were used to calculate, respectively, the surface area and pore volume from the acquired N\textsubscript{2} isotherms. The crushing strength of the oxygen carriers was obtained by measuring the force required to break the oxygen carrier particles using a Shimpo force gauge. Here, 20 measurements were
averaged to determine the mean crushing strength of the oxygen carriers. A Zeiss Leo 1530 scanning electron microscope was used to characterize the surface morphology of the freshly calcined and cycled oxygen carriers. A double-sided carbon tape was used to attach the oxygen carriers onto an aluminum holder. The oxygen carriers were sputter coated with platinum before imaging. EDX mapping was performed to analyze the surface composition of the synthesized materials.

$N_2$- and CH$_4$-TPR experiments were performed using a TGA (Mettler Toledo TGA/DSC 1) to determine the reduction characteristics of the synthesized oxygen carriers. In a typical experiment, a small quantity (~20 mg) of the oxygen carrier (53–106 µm) was heated from room temperature to 1000 ºC at a rate of 10 ºC/min under a flow of N$_2$ or 10 vol. % CH$_4$ in N$_2$ (25 mL/min). Subsequently, the sample was kept at 1000 ºC for 30 min. In all experiments, a constant N$_2$ flow of 25 mL/min was used as a purge flow over the microbalance. The reduced oxygen carriers were further characterized using Raman spectroscopy (Thermo Scientific™ DXR Raman microscope). The materials were excited with a 480 nm laser. For every material 3 spectra were taken and averaged.

5.2.3 Cyclic redox and oxygen release performance

The cyclic CLC and CLOU performance of the synthesized oxygen carriers was evaluated in a fluidized bed reactor at 900 ºC and 950 ºC, respectively. A schematic diagram of the experimental set-up is given in Appendix A1.1. In a typical experiment, Al$_2$O$_3$ was fluidized by N$_2$ with a flow rate of 2 L/min (25 ºC, 1 bar) and heated either to 900 ºC or 950 ºC. Once the temperature in the fluidized bed stabilized, 1 g of the oxygen carrier (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 (25 ºC, 1 bar) in each segment of a cycle. The duration of the oxygen release (reduction in N$_2$), reduction (in CH$_4$) and re-oxidation reactions was fixed to 120 s, 180 s and 180 s, respectively. The reactor was purged for 30 s with N$_2$ after each reaction segment. The oxygen uncoupling reaction was performed in a N$_2$ atmosphere, whereas a mixture of 10 vol. % CH$_4$ in N$_2$ was used for reduction. The oxygen carriers were oxidized using 10.5 vol. % O$_2$ in N$_2$ and air for CLOU and CLC, respectively. The moles of O$_2$, CO$_2$ and CO produced during the CLOU and CLC reactions were calculated according to:

\[ N_{O_2} = V_{N_2} \times \int \frac{y_{O_2}}{1 - y_{O_2}} \, dt \]  

(5.1)
\[ N_{\text{CO}_2} = V_{\text{CH}_4/\text{N}_2} \times \int y_{\text{CO}_2} \, dt \]  

(5.2)

\[ N_{\text{CO}} = V_{\text{CH}_4/\text{N}_2} \times \int y_{\text{CO}} \, dt \]  

(5.3)

where \( N_{O_2} \), \( N_{CO} \) and \( N_{CO} \) are, respectively, the number of moles of \( O_2 \), \( CO_2 \) and \( CO \) produced in each cycle. \( V_{\text{N}_2} \) and \( V_{\text{CH}_4/\text{N}_2} \) are the molar flow rates of \( N_2 \) and 10 vol. % \( CH_4 \) in \( N_2 \) and \( y_{O_2} \), \( y_{CO_2} \) and \( y_{CO} \) are the mole fractions of \( O_2 \), \( CO_2 \) and \( CO \) in the dried off-gases, respectively.

5.3 Results

5.3.1 Characterization of the as-synthesized (calcined) oxygen carriers

\[ \text{Cu50Ce} \quad \text{Cu60Ce} \quad \text{Cu50Al} \]

\[ 20^{\circ} \]

\[ \text{Normalized intensity} \]

\[ \text{Figure 5.1. X-ray diffractograms of the freshly calcined oxygen carriers. The following compounds were identified: (●) CuO, (●) CeO}_{2-x} \text{ and (■) CuAl}_{2}O_{4}.} \]

The crystalline phases of the calcined oxygen carriers were determined using XRD. The XRD patterns of \( \text{CeO}_{2-x} \)-stabilized \( \text{CuO} \) (50 and 60 wt. %) and the reference material, \( i.e. \) \( \text{Al}_2\text{O}_{3} \)-stabilized \( \text{CuO} \) (50 wt. %) are plotted in Figure 5.1. In the oxidized state the \( \text{CuO-CeO}_{2-x} \) oxygen carriers are composed of the monoclinic and cubic fluorite structure of, respectively, \( \text{CuO} \) and \( \text{CeO}_{2-x} \). The diffractograms show only peaks due to \( \text{CeO}_{2-x} \) and \( \text{CuO} \).
The formation of solid solutions between CuO and CeO$_{2-x}$ could not be observed, confirming the chemical stability of CeO$_{2-x}$ in this configuration. The diffractogram of Al$_2$O$_3$-stabilized CuO (50 wt. % CuO) reveals, in addition to the presence of CuO, the formation of the spinel CuAl$_2$O$_4$ (cubic structure). Peaks characteristic of Al$_2$O$_3$ were not observed in the calcined material. The average crystallite sizes of CuO, CeO$_{2-x}$ and CuAl$_2$O$_4$ in the oxygen carriers are given in Table 5.1 along with the values of the surface area, pore volume and crushing strength of the materials. From Table 5.1 it can be seen that the crystallite size of CuO was very similar in all of the oxygen carriers synthesized. N$_2$ adsorption measurements confirm that the high calcination temperature of 1000 °C yielded oxygen carriers with a low surface area and pore volume. It is worth mentioning here again that a low surface area and pore volume do not necessarily have a detrimental effect on the redox characteristics of CuO-based oxygen carriers (see also Chapter 2). The crushing strength of all oxygen carriers was in the range 10.9–12.9 N. These crushing strengths are sufficiently high to allow fluidized bed operation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu50Ce</th>
<th>Cu60Ce</th>
<th>Cu50Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area [m$^2$/g]</td>
<td>&lt; 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore volume [cm$^3$/g]</td>
<td>&lt; 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crushing strength [N]</td>
<td>12.9 ± 1.6</td>
<td>10.9 ± 1.9</td>
<td>12.3 ± 2.8</td>
</tr>
<tr>
<td>CuO (200) [nm]</td>
<td>30</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>CeO$_{2-x}$ (111) [nm]</td>
<td>52</td>
<td>59</td>
<td>-</td>
</tr>
<tr>
<td>CuAl$_2$O$_4$ (311) [nm]</td>
<td>-</td>
<td>-</td>
<td>49</td>
</tr>
</tbody>
</table>

SEM was used to analyze the surface morphology of the calcined oxygen carriers. Figures 5.2(a) and (b) show that the surface of Cu50Ce and Cu60Ce was composed of tightly packed polyhedrons. EDX analysis of Cu50Ce confirmed that CuO and CeO$_{2-x}$ were uniformly distributed in the oxygen carrier. On the other hand, a phase separation between CuO and CeO$_{2-x}$ was observed for Cu60Ce. Turning to Al$_2$O$_3$-stabilized CuO, the surface of Cu50Al was comparatively smooth and composed in parts of small grains, see Figure 5.2(c). EDX mapping of the surface of Cu50Al revealed that the small grains contain mostly CuO, whereas the smooth structures are a mixture of CuO and Al$_2$O$_3$. The heterogeneous
distribution of CeO$_{2-x}$ in Cu60Ce and CuAl$_2$O$_4$ in Cu50Al may affect negatively the stability of these materials.

Figure 5.2. Scanning electron micrographs and the corresponding EDX maps of the oxygen carriers calcined at 1000 °C: (a) Cu50Ce, (b) Cu60Ce and (c) Cu50Al.

5.3.2 Temperature programmed reduction

To investigate the oxygen release (uncoupling) characteristics of the calcined oxygen carriers, TPR experiments were performed in a N$_2$ atmosphere. For comparison the N$_2$-TPR characteristics of pure, *i.e.* unsupported, CuO, and CeO$_{2-x}$ are also plotted in Figure 5.3(a). The onset of the reduction reaction was defined as the temperature at which the oxygen carrier had lost 2 % of the total weight loss. Similarly, the reduction reaction was considered as completed once 98 % of the total weight loss had been reached. The reduction of CuO in N$_2$ (4CuO → 2Cu$_2$O + O$_2$) started at ~737 °C and was completed at ~946 °C. On the other hand, CeO$_{2-x}$ did not reduce in the temperature range studied here. The reduction of CeO$_{2-x}$-stabilized CuO started at a slightly higher temperature (~775 °C), but was completed at a significantly lower temperature (~895 °C) when compared to unsupported CuO. Reducing the weight fraction of CuO in CuO-CeO$_{2-x}$ led to a further decrease of the reduction
temperature: a very favorable characteristic with regards to CLOU applications. XRD analysis confirmed that also in the reduced oxygen carrier mixing between CeO$_{2-x}$ and Cu$_2$O did not occur (Figure 5.3(b)). In contrast, the reduction of Cu50Al started at a substantially higher temperature (~827 °C) when compared to CeO$_{2-x}$-stabilized CuO or pure CuO. The reduction of Cu50Al was only completed once the final temperature of 1000 °C was reached. The shift of the reduction temperature to higher temperatures for Cu50Al can be explained by the presence of CuAl$_2$O$_4$ that reduces (slowly) according to:

$$4\text{CuAl}_2\text{O}_4 \rightarrow 4\text{CuAlO}_2 + 2\text{Al}_2\text{O}_3 + \text{O}_2$$ (5.4)

The X-ray diffractogram of reduced Cu50Al (Figure 5.3(b)) confirmed the presence of CuAlO$_2$ and Al$_2$O$_3$. Thus, owing to its high chemical stability (i.e. no phase intermixing) and, in turn lower reduction temperature, CeO$_{2-x}$-stabilized CuO is superior to Al$_2$O$_3$-stabilized CuO. The CuO content of the oxygen carriers, determined through the weight loss recorded during reduction, is given in Table 5.2. For all of the oxygen carriers synthesized, the CuO content determined via N$_2$-TPR is close to the theoretically expected values.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu50Ce</th>
<th>Cu60Ce</th>
<th>Cu50Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO content [wt. %]</td>
<td>52</td>
<td>60</td>
<td>51</td>
</tr>
</tbody>
</table>
Figure 5.3. (a) N$_2$-TPR profiles of the synthesized oxygen carriers: (—) CuO, (—) Cu50Ce, (—) Cu60Ce, (—) Cu50Al and (—) CeO$_{2-x}$. (b) X-ray diffractograms of the reduced oxygen carriers. The following compounds were identified: (●) Cu$_2$O, (♦) CeO$_{2-x}$, (■) CuAlO$_2$ and (▲) Al$_2$O$_3$.

CH$_4$-TPR and Raman spectroscopy of CeO$_{2-x}$- or Al$_2$O$_3$-supported CuO, pure CuO and pure CeO$_{2-x}$ were utilized to determine their reduction characteristics and pathways and the extent of carbon deposition. The CH$_4$-TPR profiles, Figure 5.4(a), show that the reduction
of unsupported CuO occurred in the temperature range 535–895 °C via an apparent single step reaction, \( \text{viz.} \):

\[
4\text{CuO} + \text{CH}_4 \rightarrow 4\text{Cu} + \text{CO}_2 + 2\text{H}_2\text{O} \tag{5.5}
\]

Once CuO was fully reduced to metallic Cu, no further increase in sample weight (a weight increase would indicate carbon deposition) was observed. Nonetheless, the Raman spectrum, Figure 5.4(b), of the reduced material showed minor peaks at 1360 cm\(^{-1}\) and 1582 cm\(^{-1}\) that are characteristic for graphite. Raman spectroscopy is expected to have a higher sensitivity to carbon deposition than thermogravimetry. The peak located at 1360 cm\(^{-1}\) originates from defects in the graphite structure, whereas the peak located at 1582 cm\(^{-1}\) corresponds to the deformation of carbon bonds in the basal planes of the hexagonal structure of graphite.\(^{107-109}\) Nonetheless, owing to the comparatively small peak height, Raman measurements indicate that unsupported Cu has a small tendency for carbon deposition \( \text{via} \):

\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \tag{5.6}
\]

The CH\(_4\)-TPR experiments reveal further that CeO\(_{2-x}\) is slowly reducing to CeO\(_3\) in a CH\(_4\) atmosphere. The reduction starts at \( \sim 765 \) °C, but was not completed within the measurement time (even for a holding time of 30 min at 1000 °C). Both CeO\(_3\) and CeO\(_{2-x}\) were identified in the X-ray diffractogram of the reduced material. Furthermore, Raman analysis confirmed that no carbon was deposited on pure CeO\(_{2-x}\). Turning to CeO\(_{2-x}\)-stabilized CuO, its reduction started at \( \sim 490 \) °C, \( \text{i.e.} \) at a lower temperature compared to pure CuO, and progressed \( \text{via} \) a two-step mechanism. The first reduction step occurred in the temperature range 490–735 °C 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 \( \text{via} \) reaction 5.6. The CH\(_4\)-TPR profile of Cu50Al shows 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 °C. At the end of the CH\(_4\)-TPR experiment again an increase in sample weight is observed.
Figure 5.4. (a) CH₄-TPR profiles and (b) Raman spectra of the reduced oxygen carriers: (—) CuO, (—) Cu50Ce, (—) Cu60Ce, (—) Cu50Al and (—) CeO₂ₓ.
5.3.3 CLC and CLOU performance

**Figure 5.5.** (a) Quantity of oxygen released as determined in a fluidized bed at 950 °C in N₂: (●) Cu50Ce, (▲) Cu60Ce and (■) Cu50Al. The duration of the reduction and re-oxidation reactions was fixed to 120 s and 180 s, respectively. The dashed and dotted horizontal lines indicate the theoretical oxygen uncoupling capacity of oxygen carriers that contain 50 wt. % and 60 wt. % CuO, respectively. (b) Concentration of O₂ (Cu50Ce) in the sampled off-gas stream as a function of time (first six cycles).
The cyclic oxygen uncoupling capacity and the partial pressure of the oxygen released by the different materials synthesized were determined in a fluidized bed at 950 °C. Figure 5.5(a) plots the moles of O₂ released by the reduction of 1 g of oxygen carrier in a N₂ atmosphere as a function of cycle number. For Cu50Ce and Cu60Ce, the amount of O₂ released during the first cycle was lower than the theoretically expected value since Cu50Ce and Cu60Ce were not fully reduced during the first cycle (a fixed reduction time of 120 s was used). This was confirmed by analyzing the composition of the off-gas (Figure 5.5(b)). Nonetheless, the rate of O₂ release increased with cycle number, resulting in a gradual increase in the amount of O₂ released over the first 6 cycles. Starting from the sixth cycle, the oxygen carriers were fully reduced within the given reduction time (120 s), thus, yielding an oxygen release very close to the theoretically expected value.

On the other hand, Cu50Al possessed a stable, but very low oxygen uncoupling capacity of only 0.18 mmol O₂/gOC, i.e. ~88 % lower than the theoretically expected value of 1.6 mmol O₂/gOC. The low oxygen uncoupling capacity of Cu50Al is due to the slow reduction of CuAl₂O₄ in N₂ as observed previously in the N₂-TPR experiments.

The concentration of the O₂ released by Cu50Al and Cu50Ce during the tenth CLOU cycle is plotted in Figure 5.6. The decomposition of Cu50Ce started once the oxygen concentration in the fluidized bed had reached ~2.4 mol/m³. This somewhat higher O₂ concentration than the thermodynamically predicted value (~1.6 mol/m³ at 950 °C) can be explained by the fact that the previous exothermic oxidation step had caused an increase in the bed temperature by ~15 °C. The continuous decrease in the O₂ concentration with measurement time is due to the fact that only 1 g of oxygen carrier was used in the fluidized bed experiments. Nonetheless, Figure 5.6(a) demonstrates that CeO₂ₓ-stabilized CuO can provide an O₂ atmosphere very close to the theoretically predicted equilibrium concentration. In experiments using Cu50Al, the O₂ concentration decreased in a similar manner as in the blank experiment (i.e. using a fluidized bed without any oxygen carrier) owing to the slow rate of O₂ release of CuAl₂O₄ (Figure 5.6(b)).
Figure 5.6. Concentration profile of the O$_2$ released during the tenth reduction step: (a) Cu50Ce and (b) Cu50Al. The experiment was performed in a fluidized bed at 950 °C. The dotted line (··········) plots the oxygen concentration in a blank experiment, whereas the horizontal dashed lines (— —) correspond to the equilibrium oxygen concentration at 950 °C and 965 °C.
Figure 5.7. Off-gas composition during the tenth redox cycle performed in a fluidized bed at 900 °C: (a) Cu50Ce and (b) Cu50Al: (—) CH₄, (—) CO₂, (—) CO and (—) O₂. A mixture containing 10 vol. % CH₄ in N₂ was used to reduce the oxygen carrier. The reduction time was fixed to 180 s.

The cyclic redox characteristics of the oxygen carriers synthesized were assessed in a fluidized bed at 900 °C using methane for reduction (10 vol. % CH₄ and 90 vol. % N₂). The composition of the off-gas during the tenth redox cycle is plotted in Figures 5.7(a) and (b) for Cu50Ce and Cu50Al, respectively. In Figure 5.7(a) it can be seen that at the time when the atmosphere was switched from air to N₂, the mole fraction of O₂ stabilized at
~0.012 owing to the spontaneous reduction of CuO to Cu$_2$O. The mole fraction of O$_2$ was close to the thermodynamically predicted equilibrium mole fraction of oxygen at 900 °C, viz. 0.014. Switching the atmosphere from N$_2$ to CH$_4$ resulted in a sharp rise in the mole fraction of CH$_4$. The inset in Figure 5.7(a) shows clearly an induction period for the reduction of Cu50Ce with CH$_4$. After the induction period, the mole fraction of CH$_4$ decreased as CH$_4$ reacted with CeO$_{2-x}$-stabilized CuO producing CO$_2$, CO and H$_2$O. Upon re-oxidation of the reduced oxygen carrier a small CO$_2$ peak was recorded. This is indicative of carbon deposition via reaction 5.6 albeit occurring only to a small extent.

On the other hand, for Cu50Al the mole fraction of the O$_2$ released was found to drop continuously when switching the atmosphere form air to N$_2$, see Figure 5.7(b). This behavior is explained by the slow release of oxygen by CuAl$_2$O$_4$, as noted previously (Figure 5.6(b)). After switching from N$_2$ to a CH$_4$ atmosphere, the mole fraction of CO$_2$ increased rapidly. The inset in Figure 5.7(b) confirms that Cu50Al reacts instantaneously with CH$_4$, i.e. unlike for CeO$_{2-x}$-stabilized CuO an induction period is not observed for Cu50Al. Similar to Cu50Ce, during reduction the CO$_2$ peak is followed by a CO peak, as 'oxygen depleted' Cu50Al is only oxidizing partially CH$_4$. When compared to Cu50Ce, for Cu50Al a large CO$_2$ peak was observed during re-oxidation in air. This is indicative of a high quantity of carbon deposited on Cu50Al.

Assuming the complete oxidation of CH$_4$ to CO$_2$, the normalized yield of CO$_2$ is defined as:

$$\text{Normalized yield of CO}_2 = \frac{\text{moles of CO}_2 \text{ measured}}{\text{theoretically expected moles of CO}_2 \text{ produced}}$$

(5.7)

The normalized yield of CO$_2$ as a function of cycle number is plotted in Figure 5.8. For Cu50Ce and Cu60Ce the normalized yield of CO$_2$ is stable and reaches, respectively, ~0.85 and ~0.95 over the 25 redox cycles tested. Normalized yields less than 1 are due to the formation of CO during reduction, see Figure 5.7(a). It is important to mention here that Cu60Ce agglomerated during the 25 redox cycles test. On the other hand, for Cu50Al the average normalized yield of CO$_2$ was ~0.85 during the 25 redox cycles tested. This low yield of CO$_2$ can again be explained by the partial oxidation of CH$_4$ at the end of the reduction step as shown in Figure 5.7(b).
Figure 5.8. Normalized yield of CO$_2$ as a function of cycle number as 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.

Figure 5.9. Moles of carbon deposited via CH$_4$ decomposition during CLC operation in a fluidized bed at 900 °C as a function of cycle number: (●) Cu50Ce, (▲) Cu60Ce and (■) Cu50Al. The duration of the reduction reaction was fixed to 180 s.

Turning now to carbon deposition, Figure 5.9 plots the quantity of carbon deposited during CH$_4$ reduction. Cu50Ce showed a comparatively low tendency for carbon deposition, whereas the quantity of carbon deposited on Cu60Ce increased with cycle number.
For Cu50Al, an approximately three times higher quantity of carbon deposited was observed than for Cu50Ce.

Figure 5.10. (a) Composition of the off-gases during the tenth redox cycle at 900 °C for Cu50Ce: (—) CH₄, (—) CO₂, (—) CO and (—) O₂. A mixture containing 10 vol. % CH₄ in N₂ was used to reduce the oxygen carrier. The reduction time was fixed to 30 s. (b) Moles of CO₂ produced as a function of cycle number.

A high CO selectivity during reduction and a large quantity of carbon deposited would reduce the energetic efficiency and the CO₂ capture efficiency of the process.
From Figure 5.7(a) it can be seen that for Cu50Ce the formation of CO and the deposition of carbon can be avoided by a judicious choice of the reduction time. In fact, when the duration of the reduction segment was reduced from 180 s to 30 s, CO and carbon deposits were not observed, see Figure 5.10(a). The moles of CO₂ produced, when the reduction time was reduced to 30 s, are plotted in Figure 5.10(b). Over the first 10 cycles, the moles of CO₂ produced increased with cycle number, stabilizing after the tenth cycle at 1.43 mmol CO₂. It should be noted that this quantity of CO₂ produced is very close to the theoretically expected value of 1.57 mmol CO₂ for the CuO–Cu₂O transition. Indeed, the trend observed in Figure 5.10(b) is similar to the trend observed for the release of O₂ under CLOU conditions (Figure 5.5(a)). This indicates that for a short reduction time, CH₄ is primarily oxidized with molecular oxygen released through the CuO-Cu₂O transition.

5.4. Discussion

5.4.1 Reduction mechanism of oxygen carriers synthesized

The reduction of CeO₂₋ₓ-stabilized CuO in a CH₄ atmosphere occurs via a two-step mechanism (Figure 5.4). To elucidate the detailed reduction mechanism of CeO₂₋ₓ-stabilized CuO, CH₄-TPR experiments were stopped at 735 ºC and 850 ºC, as marked in Figure 5.4(a). Subsequently, the partially reduced oxygen carriers were analyzed using XRD and Raman spectroscopy. The X-ray diffractograms of Cu50Ce, Figure 5.11(a), revealed that in the first reduction step CuO was reduced to Cu, whereas in the second reduction step CeO₂₋ₓ was partially reduced to Ce₂O₃. The Raman spectra acquired, Figure 5.11(b), allowed us to elucidate further the prevailing near-order cationic-anionic lattice changes occurring in ceria during reduction. CeO₂₋ₓ, due to its cubic symmetry, has a single, characteristic Raman F₂g stretching mode for the cationic-anionic vibrations (peak at around ~463.3 cm⁻¹ for 700 ºC). This is in agreement with previously reported values.¹⁹, ¹¹⁰-¹¹² Changes in the bulk cationic-anionic bond strength of CeO₂₋ₓ as a function of reduction temperature, were determined by assessing the shift in the F₂g peak position, see insets in Figure 5.11(b). A significant blue shift of the F₂g stretching mode wavenumber (by ~1.8 cm⁻¹) with increasing reduction temperature was observed.¹¹³ The observed blue shift is indicative of a lattice expansion of bulk CeO₂₋ₓ owing to its partial reduction to Ce₂O₃.⁸¹, ¹¹⁴ Furthermore, no Raman peaks corresponding to carbon (1361 cm⁻¹ and 1583 cm⁻¹) were observed at 735 ºC and 850 ºC, indicating that carbon deposition did not occur below 850 ºC.
Figure 5.11. (a) X-ray diffractograms of (partially) reduced Cu50Ce. The following compounds were identified: (●) Cu, (♦) CeO$_{2-x}$ and (▲) Ce$_2$O$_3$. (b) Raman spectra of (partially) reduced Cu50Ce: (—) $T = 735 ^\circ$C, (—) $T = 850 ^\circ$C and (—) $T = 1000 ^\circ$C, 30 min.
Figure 5.12. (a) X-ray diffractograms of (partially) reduced Cu50Al. The following compounds were identified: (●) Cu, (■) CuAl$_2$O$_4$ and (□) Al$_2$O$_3$. (b) Raman spectra of (partially) reduced Cu50Al: (—) $T = 810$ °C, (–) $T = 850$ °C, (—) $T = 970$ °C and (—) $T = 1000$ °C, 30 min.

To understand better the CH$_4$-TPR profile of Cu50Al, additional XRD and Raman spectroscopy were performed at the temperatures marked in Figure 5.4(a), viz. 810 °C, 850 °C and 970 °C. Both at 810 °C and 860 °C, Cu and CuAl$_2$O$_4$ were identified in the X-ray diffractograms (Figure 5.12(a)) of partially reduced Cu50Al. The intensity of the CuAl$_2$O$_4$
peaks was found to decrease with increasing temperature due to its slow reduction to Cu and Al$_2$O$_3$. On the other hand, Raman spectroscopy confirmed that graphite formed on the partially reduced Cu50Al (810 °C and 860 °C), see Figure 5.12(b). Figure 5.12(b) also reveals, as expected, an increase in the intensity of the graphite peaks with increasing temperature. These measurements confirm that Cu50Al has a higher tendency for carbon formation than CeO$_{2-x}$-supported CuO. Combining the results of the XRD, Raman and CH$_4$-TPR measurements of Cu50Al allows the conclusion that in the temperature range 810–860 °C the rate of carbon deposition was higher than the rate of reduction. Intriguingly, between 860 °C and 970 °C, only a slight increase in the intensity of the graphite peaks (Figure 5.12(b)) was observed suggesting 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, due to the very slow reduction of CuAl$_2$O$_4$. This reduction step was completed at ~970 °C. The X-ray diffractogram of Cu50Al sampled at 970 °C or 1000 °C (after a holding time of 30 min) showed only peaks due to Cu and Al$_2$O$_3$. Finally, the increase in weight from 970 °C until the end of the CH$_4$-TPR experiment was due to additional carbon deposition, as confirmed by Raman spectroscopy.

5.4.2 Increase in reduction rate with cycle number

Figures 5.5 and 5.10(b) show that the (apparent) rate of reduction of CeO$_{2-x}$-stabilized CuO increases with cycle number under CLOU conditions. To elucidate the reason for the increasing reduction rate with cycle number, the BET surface areas of the cycled oxygen carriers were measured and found to be < 0.5 m$^2$/g. From Table 1 it can be seen that the surface area of the fresh oxygen carriers was also < 0.5 m$^2$/g. Thus, the increasing rate of O$_2$ release with cycle number cannot be attributed to changes in the surface area. Therefore, it can be speculated that the increasing rate of the reduction reaction with cycle number is due to an increasing structural disorder in the material, facilitating, in turn the transport and release of O$_2$, as discussed previously in Chapter 4.

5.4.3 Agglomeration and carbon deposition characteristics

The agglomeration of oxygen carriers is a serious concern since it can lead to de-fluidization. A possible explanation for the agglomeration of Cu60Ce is the phase separation of CuO and CeO$_{2-x}$ during calcination (Figure 5.2(b)). No phase separation (Figure 5.2(a)) and hence no agglomeration was observed for Cu50Ce. It is worth mentioning here that Hedayati et al.$^{103}$
did not observe any significant agglomeration of CeO$_{2-x}$- or Ce$_{0.9}$Gd$_{0.1}$O$_{2-x}$-supported CuO (60 wt. % CuO) probably because Hedayati et al.\textsuperscript{103} performed only three redox cycles which are insufficient to assess the agglomeration characteristics of CeO$_{2-x}$-supported, CuO-based oxygen carriers containing 60 wt. % CuO. Thus, the experiments performed here suggest that the maximal loading of CuO in CeO$_{2-x}$-supported CuO should be limited to $\sim$50 wt. %.

The low quantity of carbon deposited on Cu50Ce (Figure 5.9) can be explained by the ability of surface oxygen of CeO$_{2-x}$ to react with carbonaceous species according to:\textsuperscript{115, 116}

\[ nC + CeO_{2-x} \rightarrow CeO_{2-x:n} + nCO \quad (5.8) \]

On the other hand, the quantity of carbon deposited on Cu60Ce increased with cycle number. Currently, the decreasing coke resistance of Cu60Ce with cycle number cannot be explained unequivocally. A possible explanation might be that severe agglomeration in Cu60Ce reduces the quantity of surface oxygen required for the removal of carbonaceous species. As discussed in section 5.4.1, for Cu50Al the decomposition of CH$_4$ started during CuO reduction, explaining the large quantity of carbon deposited.

5.5 Conclusions

In this Chapter, the suitability of CeO$_{2-x}$-stabilized CuO for CLC and CLOU is demonstrated. This class of material is able to remove effectively carbon precursors, thus, minimizing carbon deposition. XRD analysis confirmed that no solid solutions were formed for CuO-CeO$_{2-x}$ oxygen carriers. CH$_4$-TPR revealed that CeO$_{2-x}$-stabilized CuO reduced through a two-step mechanism. In the first step only CuO is reduced to Cu, whereas in the second step CeO$_{2-x}$ was reduced to CeO$_{2-x}$/Ce$_2$O$_3$. Importantly, no carbon deposition was observed during CuO reduction with CH$_4$. Raman analysis of the anionic-cationic bonding of CeO$_{2-x}$ revealed that the oxygen non-stoichiometry is increased during CH$_4$ reduction and that lattice oxygen (released by CeO$_{2-x}$) contributes to the increased resistance to carbon formation of these materials. In contrast, Al$_2$O$_3$-stabilized CuO reduced via a single step and significant carbon deposition was observed.

Cyclic CLOU experiments, performed at 950 °C in a fluidized bed, revealed that the partial pressure of the O$_2$ released by CeO$_{2-x}$-stabilized CuO was very close to the thermodynamically predicted value. The cyclic O$_2$ release of CeO$_{2-x}$-stabilized CuO was initially low but increased with cycle number, reaching the theoretically expected value after five cycles. On the other hand, Al$_2$O$_3$-stabilized CuO showed a very low cyclic O$_2$ release.
owing to the slow rate of CuAl2O4 decomposition. Under CLC conditions, all oxygen carriers synthesized showed stable CO2 yields. However, CeO2-x-stabilized CuO containing 60 wt. % CuO was found to agglomerate most likely due to phase separation between CuO and CeO2-x. Importantly, CeO2-x-stabilized CuO showed an approximately three times lower quantity of carbon deposited when compared to Al2O3-stabilized CuO. Owing to their high and stable quantity of O2 released, the high equilibrium partial pressure of O2 and the high resistance to carbon deposition and agglomeration, CeO2-x-stabilized CuO containing 50 wt. % CuO was identified as a promising material for CLC- and CLOU-based CO2 capture processes.
Chapter 6

The influence of the presence of a CuO percolation network on the oxygen release and re-oxidation kinetics of CuO

6.1 Introduction

The CLC performance of a supported oxygen carrier depends critically on the activation energy for the conduction of oxygen anions and electrons, since the redox reactions are rate limited by the diffusion of oxygen anions.\textsuperscript{117} Besides increasing the sintering resistance of a material, the support can also enhance the transport of charge carriers within an oxygen carrier particle.\textsuperscript{89, 118} To transport oxygen anions and electrons through an oxygen carrier particle, a three-dimensional continuous network of electrically conductive pathways is required (percolation network).\textsuperscript{119, 120} At the percolation threshold, often \textasciitilde 30–40 vol. % of the conducting component in a binary mixture, a sharp drop in the electrical resistance of the material is observed due to the formation of conductive pathways.\textsuperscript{119, 121, 122} Thus, the degree of percolation could be used as a tool to improve the redox characteristics of an oxygen carrier. However, the effect of the formation of a percolation network in an oxygen carrier on the rate of the redox reactions has not been investigated previously. In this Chapter, the electrical conductivity and the rate of oxidation of a transition metal oxygen carrier as a function of its percolation degree was probed. To this end, systematic experiments were performed on model materials that contain CuO and ceria (CeO\textsubscript{2-x}) in a mixture in the range 20–60 wt. % CuO. The degree of percolation of CuO in the oxygen carriers was visualized using energy dispersive X-ray spectroscopy. Additionally, 4-point direct current (DC) conductivity measurements were used to determine the electrical conductivity characteristics of the materials synthesized. Finally, the oxidation kinetics of the oxygen carriers was studied in a thermogravimetric analyzer at 700 °C. Using these detailed experiments on model
oxygen carriers, it was possible to demonstrate that the oxygen release and uptake characteristics depend critically on the charge transport pathways in an oxygen carrier particle.

6.2 Experimental

6.2.1 Oxygen carrier synthesis

A modification of the co-precipitation technique originally reported by He et al. was used to synthesize CeO$_2$-supported CuO that contained 20, 30 or 60 wt. % CuO. In a typical synthesis, appropriate amounts of Cu(NO$_3$)$_2$·2.5H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O were dissolved in 400 mL of deionized water (15 MΩ.cm). Subsequently, 400 mL of an aqueous solution containing 24 g NaOH and 6 g Na$_2$CO$_3$ was added dropwise to the nitrate solution under continuous stirring. After adjusting the pH of the resulting slurry to 8.5 using NaOH, the mixture was heated to 80 °C and kept at 80 °C for 15 h under reflux. The resulting precipitate was filtered and washed with deionized water until the electrical conductivity of the filtrate was < 100 μS/cm. The cake of the washed precipitate was dried in an oven at 100 °C for 24 h and subsequently calcined in a muffle furnace at 1000 °C for 2 h (temperature ramp of 5 °C/min). The calcined materials were crushed and sieved into two different size ranges, viz. 300–425 µm and 106–150 µm. Throughout this Chapter, the abbreviation Cu$_x$Ce, where $x$ is the wt. % of CuO, will be used to refer to the different materials synthesized.

6.2.2 Oxygen carrier characterization

A Bruker D8 Advance X-ray diffractometer was used to determine the chemical composition of the freshly calcined and reduced materials. The diffractogram was mounted with a Lynx eye super speed detector and operated at 40 mA and 40 kV using Cu K$_\alpha$ radiation ($\lambda = 1.5418$ nm). Each sample was scanned within the range of $20 = 20–80^\circ$ using a step size of 0.0275$^\circ$ per second. The average crystallite sizes of CuO and CeO$_2$-x were estimated using the Scherrer equation. The surface area and pore volume of the synthesized materials were calculated using, respectively, the Brunauer et al. and Barrett et al. models. A Quantachrome NOVA 4000e analyzer was used to measure the N$_2$ adsorption and desorption isotherms of the synthesized materials at -196 °C. Each sample was degassed for 3 h at 300 °C prior to the measurement. The surface morphology of the freshly calcined oxygen carriers was characterized using a scanning electron microscope (Zeiss LEO 1530 FEG) operated at 20 kV. The elemental composition of the surface was mapped using EDX
spectroscopy. N\textsubscript{2}-TPR experiments were performed in a Mettler Toledo TGA (TGA/DSC 1). In a typical experiment, \textasciitilde15 mg of the material was heated from room temperature to 1000 °C at a rate of 10 °C/min under a flow of 100 mL/min of N\textsubscript{2} and kept at 1000 °C for 30 min. In all experiments, a constant N\textsubscript{2} flow of 25 mL/min was used as purge flow over the micro-balance.

4-point DC conductivity measurements were used to measure the electrical conductivity of the synthesized materials. First, the materials were crushed and pelletized by uni-axial (40 kN for 2 min) and isostatic (1000 kN for 2 min) pressing. The pellets were calcined at 1000 °C for 24 h using a heating and cooling rate of 2 °C/min. The sintered pellets possessed a density of > 95 % of the theoretical density. Platinum electrodes were painted on both sides of the pellets using platinum paste (C 3605 P, Heraeus GmbH). Subsequently, platinum wires were fixed in a 4-point electrode arrangement to the pellet using a ceramic binder.\textsuperscript{76} The resistance of each pellet was measured in air as a function of temperature (from 25 °C to 950 °C using a heating and cooling rate of 3 °C/min) by applying a DC voltage of 1 V (Keithley 2601B SMU). To ensure reproducibility, three heating and cooling cycles were performed.

6.2.3 Oxidation kinetics

The rate of oxidation of CeO\textsubscript{2-x}-supported Cu was measured in a TGA at 700 °C. A mixture of 10 vol. % H\textsubscript{2} in N\textsubscript{2} was used for reduction, whereas re-oxidation was performed with 10.5 vol. % O\textsubscript{2} in N\textsubscript{2}. The reaction chamber was purged with N\textsubscript{2} for 30 s after each reduction and oxidation segment. The total flow rate of the gases in each reaction segment was 175 mL/min, as measured at 25 °C and 1 bar (including the 25 mL/min purge flow, N\textsubscript{2}, over the microbalance). In a typical experiment, \textasciitilde5 mg of the material was placed in an alumina crucible and heated to 700 °C in air. After stabilization of the temperature, the flow of air was switched off and the material was reduced in H\textsubscript{2} for 120 s. Subsequently, the sample was re-oxidized in O\textsubscript{2} for 120 s and the process was repeated twenty times to assess whether the redox characteristics varied with cycle number.
6.3 Results

6.3.1 Composition and morphology of the as-synthesized oxygen carriers

Figure 6.1. X-ray diffractograms of the as-synthesized (calcined) oxygen carriers: (—) Cu20Ce, (—) Cu30Ce and (—) Cu60Ce. The following compounds were identified: (♦) CeO$_{2-x}$ and (○) CuO.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu20Ce</th>
<th>Cu30Ce</th>
<th>Cu60Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area [m$^2$/g]</td>
<td></td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td>Pore volume [cm$^3$/g]</td>
<td></td>
<td>&lt; 0.01</td>
<td></td>
</tr>
<tr>
<td>CuO (111) [nm]</td>
<td>31</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>CeO$_{2-x}$ (111) [nm]</td>
<td>79</td>
<td>75</td>
<td>58</td>
</tr>
</tbody>
</table>

XRD confirms that the materials synthesized contain CuO and CeO$_{2-x}$ (Figure 6.1). The average crystallite sizes of CuO and CeO$_{2-x}$ were estimated from the (111) and (111) crystal planes of CuO and CeO$_{2-x}$, respectively. Table 6.1 summarizes the crystallite sizes, surface area and pore volume of the materials. It was found that the crystallite size of CuO...
was affected negligibly by the composition of the material. On the other hand, the average crystallite size of the ceramic phase, $\text{CeO}_{2-x}$, decreased with increasing $\text{CuO}$ content by up to 25%. Owing to the high calcination temperature of 1000 °C, the synthesized materials possessed a relatively low surface area (< 1 m$^2$/g) and pore volume (< 0.01 cm$^3$/g).

Figure 6.2. Scanning electron micrographs and the corresponding EDX maps of the oxygen carriers calcined at 1000 °C: (a, d) Cu20Ce, (b, e) Cu30Ce and (c, f) Cu60Ce. Red and yellow colors represent $\text{CuO}$ and $\text{CeO}_{2-x}$, respectively.

Scanning electron microscopy, in combination with EDX spectroscopy, was applied to analyze the surface morphology and the composition of the freshly calcined materials.
Electron micrographs (Figures 6.2(a-c)) show that the surface of the materials was composed of tightly packed micrometer-sized polyhedrons. The average size of the grains decreased with increasing quantity of CuO. For Cu20Ce, Cu30Ce and Cu60Ce an average grain size of, respectively, 2.73 ± 0.36 μm, 1.18 ± 0.27 μm and 0.88 ± 0.19 μm was determined. EDX spectra of Cu20Ce and Cu30Ce (Figures 6.2(d) and (e), respectively) show that the CeO_{2-x} grains were connected with each other. For oxygen carriers containing up to 30 wt. % CuO, CuO grains (grains with sharper corners) only decorate the surface of the CeO_{2-x} grains and do not form a percolation network. Increasing further the content of CuO in the oxygen carrier led to a higher degree of interconnectivity between the CuO and CeO_{2-x} grains. For example, in Cu60Ce both CuO and CeO_{2-x} form percolating networks, see Figure 6.2(f).

6.3.2 Conductivity measurements

The electrical conductivity (σ) of the materials as a function of temperature is plotted in Figure 6.3(a). For all of the materials the conductivity increased with temperature and CuO content. CuO is a p-type semiconductor. The increasing electrical conductivity with temperature is a characteristic of semiconductors. At a fixed temperature, the electrical conductivity was found to decrease in the following order: Cu60Ce > Cu30Ce > Cu20Ce. For example, at 700 ºC the conductivity of Cu20Ce, Cu30Ce and Cu60Ce is 0.13 S/m, 0.37 S/m and 1.15 S/m, respectively (see Figure 6.3(b)). To determine the activation energy for charge transport, the conductivity data was analyzed through an Arrhenius relationship:

\[
\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)
\]

where \( \sigma_0 \), \( k \) and \( E_a \) are, respectively, a proportionality constant, the Boltzmann constant and the activation energy for electrical conductivity. Plotting \( \ln(\sigma T) \) as a function of the reciprocal temperature (1/T) yields two regimes (Figure 6.4(a)) with distinct activation energies. Figure 6.4(b) plots the activation energies of the pure oxides, i.e. CuO and CeO_{2-x}, and the oxygen carriers as a function of the CuO content in the material. For temperatures < 450 ºC, an activation energy in the range 0.13–0.15 eV was determined for both pure CuO and the oxygen carriers. On the other hand, CeO_{2-x} had a higher activation energy for charge transport in the low temperature (\( T < 250 \) ºC) regime, viz. 0.38 eV. For temperatures exceeding 550 ºC, the activation energy for charge transport in pure CuO is 0.42 eV, see Figure 6.4(b).
At $T > 550 \, ^\circ C$, the activation energy for charge transport in Cu60Ce was 0.42 eV. Decreasing the CuO content from 60 wt. % to 20 wt. % resulted in an increase in the activation energy for charge transport from 0.42 eV to 0.80 eV. Finally, for pure CeO$_2$, an activation energy for charge transport of 1.37 eV was determined for $T > 300 \, ^\circ C$.

Figure 6.3. Electrical conductivity of the materials synthesized as a function of (a) temperature: (—) Cu20Ce, (—) Cu30Ce and (—) Cu60Ce and (b) CuO content at (●) 100 °C and (○) 700 °C.
Figure 6.4. (a) Plot of \( \ln(\sigma. T) \) as a function of reciprocal temperature for (—) Cu20Ce, (—) Cu30Ce and (—) Cu60Ce. (b) Activation energy for charge transport as a function of CuO content in (●) low \( T < 450 \, ^\circ \text{C} \) for CuCe and pure CuO and \( T < 250 \, ^\circ \text{C} \) for pure CeO\(_2\) and (○) high \( T > 550 \, ^\circ \text{C} \) for CuCe and pure CuO and \( T > 300 \, ^\circ \text{C} \) for pure CeO\(_2\).

6.3.3 Temperature programmed reduction

The oxygen release characteristics of the materials synthesized were studied in TPR experiments (in a N\(_2\) atmosphere). Figure 6.5(a) plots the normalized weight change of the
materials tested as a function of temperature. For comparison, the N$_2$-TPR characteristics of pure CuO and CeO$_{2-x}$ are also plotted in Figure 6.5(a). The reduction reaction was considered to start and finish when the material had lost 2 wt. % and 98 wt. % of the total weight loss, respectively. In the temperature range studied here, CeO$_{2-x}$ was not reduced in N$_2$ (in agreement with its Brouwer diagram).$^{124,125}$ On the other hand, the reduction of CuO (4CuO → 2Cu$_2$O + O$_2$) occurred in a single step in the temperature range 850–1000 ºC. Turning to the oxygen carriers synthesized, the reduction of CeO$_{2-x}$-stabilized CuO started at an appreciably lower temperature (~770 ºC) when compared to that of unsupported CuO. The reduction of the CuCe materials was also completed at a lower temperature when compared to pure CuO. For example, the reduction of Cu20Ce was completed at ~960 ºC (~40 ºC lower than CuO). From Figure 6.5(a) it can be seen that the (apparent) rate of reduction increases with increasing CuO content in the materials, viz. the reduction of Cu30Ce and Cu60Ce was completed at ~950 ºC and ~910 ºC, respectively. XRD confirms that only Cu$_2$O and CeO$_{2-x}$ were present in the reduced materials (Figure 6.5(b)). Since under the conditions applied here, only CuO undergoes reduction (to Cu$_2$O), the weight fraction of CuO in the materials can be determined experimentally by:

$$\text{CuO wt. fraction} = \frac{9.94(w_s - w_f)}{w_s} \quad (6.2)$$

where $w_s$ and $w_f$ are the weight of the material at the start and the end of the reduction, respectively. The factor of 9.94 is based on the stoichiometry of the reduction reaction. For all materials tested, the quantity of CuO determined by N$_2$-TPR is close to the theoretically expected values (Table 6.2).

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<thead>
<tr>
<th>Material</th>
<th>Cu20Ce</th>
<th>Cu30Ce</th>
<th>Cu60Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO content [wt. %]</td>
<td>22.9</td>
<td>30.2</td>
<td>59.7</td>
</tr>
</tbody>
</table>
Figure 6.5. (a) N$_2$-TPR profiles of the materials synthesized and (b) X-ray diffractograms of the reduced oxygen carriers: (—) CeO$_2$, (—) Cu20Ce, (—) Cu30Ce, (——) Cu60Ce and (——) CuO. The following compounds were identified: (●) Cu$_2$O and (♦) CeO$_{2-x}$.

6.3.4. Effect of particle diameter on the rate of oxidation

To assess the influence of the particle diameter on the rate of oxidation, four batches of Cu60Ce (~5 mg) with different particle sizes were oxidized with 10.5 vol. % O$_2$ in N$_2$ at 700 °C in a TGA, Figure 6.6. Only a very little difference in the measured rates of oxidations
was observed for particle diameters 106–150 µm and 150–212 µm. This observation suggests that for particle diameters < 212 µm, internal mass transfer limitations are not significant.

For particles in the size range 212–300 µm, the maximum rate dropped by ~7 % and the time required to fully oxidize the particles increased from 25 s to 33 s. This indicates that for mean particle diameters > 212 µm intra-particle mass transfer limits the rate of oxidation. For particle diameters 300–425 µm, the time required to fully oxidize the material increased further to 87 s, accompanied by a drop of ~24 % in the maximum oxidation rate, indicating significant internal mass transfer limitations. Based on the results shown in Figure 6.6, particles in the size range 106–150 µm were used in the subsequent experiments.

![Figure 6.6](image)

**Figure 6.6.** Normalized rate of oxidation of ~5 mg Cu60Ce with different particle sizes: (—) 106–150 µm, time required for complete oxidation: 22 s; (—) 150–212 µm, time required for complete oxidation: 25 s; (—) 212–300 µm, time required for complete oxidation: 33 s; (—) 300–425 µm, time required for complete oxidation: 87 s. The oxidation reaction was performed at 700 ºC under a flow rate of 150 mL/min of 10.5 vol. % O₂ in N₂ in an alumina crucible (depth 2.9 mm and diameter 5.2 mm).

### 6.3.5. Effect of particle-particle interaction on the rate of oxidation

To minimize the effect of neighboring particles on the rate of oxidation of a single particle, only a monolayer of particles was used in all of the experiments. To confirm that the reaction of a single particle was not affected by the presence of other particles, two samples of
Cu60Ce (106–150 µm, ~5 mg) were oxidized at 700 °C under identical conditions, except that the second sample was mixed with ~5 mg of alumina particles (106–150 µm) to increase the particle-particle spacing. The oxidation rates and the time required to fully oxidize the oxygen carrier were found to be very similar (Figure 6.7). Based on the results obtained it can be concluded that neighboring particles do not have an appreciable influence on the oxidation characteristics.

![Normalized rate of oxidation](image)

**Figure 6.7.** Normalized rate of oxidation of particles in the size range 106–150 µm: (—) ~5 mg Cu60Ce, time required for complete oxidation: 25 s and (—) ~5 mg Cu60Ce + ~5 mg Al₂O₃, time required for complete oxidation: 25 s. The oxidation reaction was performed at 700 °C under a flow rate of 150 mL/min of 10.5 vol. % O₂ in N₂ in an alumina crucible (depth 2.9 mm and diameter 5.2 mm).

### 6.3.6. Rate of external mass transfer on the rate of oxidation

To determine whether the oxidation rates measured in a TGA were influenced by external mass transfer limitations, the rate of external mass transfer was estimated assuming that the mass transfer in the crucible is by diffusion only. As shown in Figure 6.8 the arrangement of the sample particles in a TGA crucible resembles that of a Stefan tube. Therefore, the Stefan-Maxwell equation (equation 6.3) can be used to estimate the flux of nitrogen and oxygen between the top of the crucible and the external surface of the particles:
\[
\frac{dy_{O_2}}{dz} = -\frac{y_{N_2} N_{O_2} - y_{O_2} N_{N_2}}{c_i D}
\]  
(6.3)

Here \(y_{O_2}\) and \(y_{N_2}\) are, respectively, the mole fractions of oxygen and nitrogen, \(c_i\) is the gas concentration in the crucible, \(D\) denotes the binary molecular diffusivity of oxygen in nitrogen, \(N_{O_2}\) and \(N_{N_2}\) are the molar fluxes of oxygen and nitrogen, respectively, and \(z\) is the space coordinate (pointing from the top to the bottom of the crucible). Here it can be assumed that at the top of the crucible the mole fraction of oxygen is constant and equal to that of the bulk gas mixture, \(y_b\), passing through the TGA furnace. Furthermore, the mole fraction of oxygen at the external surface of the particles was assumed to be at thermodynamic equilibrium (\(y_{eq}\)) of the oxidation reaction \(2Cu + O_2 \leftrightarrow 2CuO\). As nitrogen is not involved in the oxidation reaction, its diffusional downward motion must be balanced by an upward bulk motion, leading to a zero nitrogen flux in the crucible.\(^{126}\) Therefore, at steady state the molar flux of oxygen from the top of the crucible to the surface of the particle is given by:

\[
N_{O_2} = \frac{D c_i}{H} \ln \left( \frac{1 - y_{eq}}{1 - y_b} \right)
\]  
(6.4)

Since the experiments were performed under isothermal conditions, it was assumed that the temperature gradient between the particles and the furnace was negligible. The mole fraction of oxygen in the bulk gas was calculated by

\[
y_b = \frac{0.209 F_r}{F_r + 0.5 F_p}
\]  
(6.5)

where \(F_r\) and \(F_p\) are the molar flow rates of the reactive and purge gases, respectively. The correction factor of 0.5 was introduced to account for the fact that only about half the purge gas is mixed with the reactive gas as it flows across the crucible (depth 2.9 mm and internal diameter 5.2 mm). The average distance, \(H\), from the top of the crucible to the surface of the particles was \(~0.5\) mm. The Fuller-Schettler-Giddings equation was used to estimate the binary diffusion coefficient.\(^{127}\) The flux of oxygen was calculated using equation 6.4 (\(y_{eq}\) is approximately zero at 700 ºC for \(2Cu + O_2 \leftrightarrow 2CuO\)).\(^{128}\) Using these values an oxygen mass flux of 0.31 mg/s was obtained. The maximum rate of external mass transfer was at least by a factor of seven higher than the rate of reaction, suggesting that external mass transfer did not limit the oxidation reaction.
Figure 6.8. Schematic diagram of a TGA crucible containing oxygen carrier particles.

6.3.7. Rate of oxidation of the materials synthesized

Figure 6.9. Normalized rate of oxidation of the Cu60Ce particles (size range 106–150 µm) as a function of cycle number: (—) first cycle, (—) second cycle, (—) third cycle, (—) fourth cycle, and (—) fifth cycle. The oxidation reaction was performed at 700 °C under a flow rate of 150 mL/min of 10.5 vol. % O₂ in N₂ in an alumina crucible with depth 2.9 mm and diameter 5.2 mm.
Figure 6.10. (a) Conversion and (b) normalized rate of oxidation of the oxygen carriers synthesized (size range 106–150 µm) as a function of time: (—) Cu20Ce, (—) Cu30Ce and (—) Cu60Ce. The oxidation reaction was performed at 700 ºC with 10.5 vol. % O₂ in N₂ (150 mL/min) using an alumina crucible (depth 2.9 mm and diameter 5.2 mm).

20 redox cycles were performed in a TGA at 700 ºC. The TGA conditions were chosen such that the rate of oxidation was not influenced appreciably by mass transfer effects. From Figure 6.9 it can be seen that the rate of oxidation of the oxygen carriers did not change significantly with cycle number. Figure 6.10(a) and (b) plot the conversion of the oxygen carriers.
carriers as a function of time and the normalized rate of oxidation as a function of time for the fifth oxidation step, respectively. The rate of oxidation was found to increase in the following order: Cu20Ce < Cu30Ce < Cu60Ce. The time required for full oxidation was determined as ~28 s, ~90 s and ~120 s for Cu60Ce, Cu30Ce and Cu20Ce, respectively. Moreover, the maximum (normalized) rate of oxidation was determined as ~0.008 mg/s/mgCu, ~0.015 mg/s/mgCu and ~0.025 mg/s/mgCu for Cu20Ce, Cu30Ce and Cu60Ce, respectively. In the case of Cu20Ce, the rate of oxidation started to decrease for $X > 0.10$. On the other hand, the oxidation of Cu30Ce and Cu60Ce continued to proceed without any significant change in the oxidation rate up to $X \sim 0.55$. For Cu60Ce, the rate of oxidation was constant even for $X < 0.90$.

6.4 Discussion

X-ray diffractograms of the as-synthesized (calcined) and reduced materials (Figures 6.1 and 6.5(b), respectively) show that CuO (or Cu$_2$O) and CeO$_{2-x}$ do not form solid solutions, thus, confirming the high chemical stability of these compounds. Electrical conductivity measurements of the oxygen carriers and the references CuO and CeO$_{2-x}$ revealed two distinct charge transport regimes, viz. a low and a high temperature regime. At low temperatures ($T < 450$ °C) the conduction in CuO is due to the hopping of charge carriers in metal deficient CuO, i.e. Cu$_{1-y}$O. Jeong and Choi determined the activation energy of charge carrier hopping in CuO as $0.1 \pm 0.01$ eV, which is in good agreement with the values obtained here ($0.13-0.15$ eV). On the other hand, at low temperatures ($T < 250$ °C) conduction in pure CeO$_{2-x}$ is due to the hopping of polarons with an activation energy of ~0.40 eV, a value that agrees very well with the 0.38 eV determined here. At high temperatures ($T > 550$ °C), the activation energy for conduction in unsupported CuO was determined previously as $0.7 \pm 0.04$ eV. This value is higher than 0.42 eV and can most likely be attributed to morphological differences between commercial CuO and the material synthesized through this work (using precipitation). The activation energy for conduction in CeO$_{2-x}$ at high temperatures is a function of grain size and has been determined as 0.99 eV, 1.35 eV and 2.80 eV for 10 nm, 30 nm and 5 μm sized grains. The pristine CeO$_{2-x}$ studied here had a grain size of ~100 nm and revealed an activation energy of 1.37 eV.

Turning now to the charge transport measurements of the synthesized oxygen carriers, Figure 6.4(b) shows that at the typical operating temperatures of the CLC process (i.e. 800–1000 °C) the activation energy for charge transport in pure CuO and Cu60Ce is
identical (0.42 eV) and ~3 times lower than in CeO$_{2-x}$. EDX mapping showed that in Cu60Ce, CuO and CeO$_{2-x}$ form a percolation network (Figure 6.2(f)). The identical values for the activation energy for charge transport in Cu60Ce and pure CuO suggests that charge transport occurs through CuO conduction bridges, forming conduction pathways with a low energy barrier. When the quantity of CuO is reduced to 30 wt. % the overall conductivity decreases (Figure 6.2(b)). However, at the same time the activation energy for charge transport increases by only 0.11 eV (Figure 6.4(b)), indicating that charge transport in Cu30Ce occurs still primarily through CuO conduction pathways. Although the EDX map of Cu30Ce shows that at the particle surface the CuO grains are not connected with each other, the conductivity data suggest that CuO conduction bridges still exist in Cu30Ce, albeit less effective than in Cu60Ce. Finally, when the CuO content in the material was decreased to 20 wt. %, the activation energy for conduction increased appreciably (from 0.53 eV to 0.80 eV) accompanied by a substantial decrease in conductivity. The sharp decrease in the conductivity indicates that the quantity of CuO in Ce20Ce is below its percolation threshold, as confirmed by EDX mapping (Figure 6.2(d)). As a consequence, charge transport occurs now predominately through CeO$_{2-x}$ conduction pathways, yielding in turn a high activation energy for charge transport in Cu20Ce (0.80 eV). The conductivity measurements reveal that the percolation threshold of CuO is between 20–30 wt. %.

From the N$_2$-TPR profiles of the synthesized materials (Figure 6.5(a)) it is evident that the rate of oxygen release increased with increasing CuO content in the material. It should be noted here that the TPR and conductivity experiments were performed in N$_2$ and air, respectively. Therefore, it is not possible to establish a relationship between the rate of oxygen release during N$_2$-TPR and the activation energy for charge transport. In order to relate the rate of oxidation to conductivity measurements, the oxidation of the reduced oxygen carriers (Cu to CuO) was performed in a TGA at 700 ºC in a kinetically controlled regime. The results show that the normalized rates of oxidation decreased in the following order: Cu60Ce > Cu30Ce > Cu20Ce. The oxidation of the oxygen carriers can be divided into two regions, viz. surface oxidation and bulk oxidation, in accordance with the finding of Chuang et al.$^{88}$ Chuang et al.$^{88}$ showed that the oxidation of Al$_2$O$_3$-stabilized Cu follows a shrinking core model. Since all materials possessed a low surface area (< 1 m$^2$/g), it is likely that the surface oxidation occurs at identical conditions for all oxygen carriers, leading in turn to very similar rates of (surface) oxidation. Once an initial CuO layer is formed around the particle, the oxidation of unreacted bulk Cu can take place either by the diffusion of gaseous oxygen through the CuO layer or by the transport of oxygen ions from the surface...
to the unreacted Cu in the bulk via CuO and/or CeO$_{2-x}$ conduction bridges. It is worth mentioning here that all materials have a low pore volume (< 0.01 cm$^3$/g), see Table 6.1, and that the rate of oxidation was not limited by intra-particle mass transfer (Figure 6.6). Therefore, it can be assumed that the oxidation of bulk Cu was not controlled by the diffusion of gaseous oxygen through CuO. Previously, using DFT calculations and inert marker experiments, Li et al.$^{90}$ have also demonstrated that solid state ionic conduction influences the rate of the redox reactions to a larger extent than the intra-particle diffusion of the reactive (or product) gas. As outlined above, CuO-based conduction pathways have a lower energy barrier for charge transport compared to CeO$_{2-x}$-based conduction pathways. Therefore, the energy barrier for solid state conduction is lowest for Cu60Ce due to the formation of a percolation network, yielding in turn the highest rate of oxidation. Decreasing the quantity of CuO in the material reduces the connectivity of CuO-CuO grain bridges, leading to an increase in the energy barrier for the transport of oxygen ions. Due to the increasing activation energy for charge transport, the rate of bulk oxidation decreases with decreasing quantity of CuO. Based on these observations, it can be concluded that for the oxidation of CeO$_{2-x}$-stabilized CuO the transport of oxygen ions from the surface to the bulk is the rate determining step. These measurements suggest that the quantity of the active transition metal oxide in the oxygen carrier should be above its percolation threshold to achieve the highest reaction rates.

6.5 Conclusions

In this Chapter, the effect of the formation of a CuO percolation network on the conduction properties and the oxidation kinetics of CeO$_{2-x}$-stabilized CuO is probed. Using a combination of EDX spectroscopy and electrical conductivity measurements it was demonstrated that the percolation threshold of CuO is between 20–30 wt. % and the activation energy for electrical conduction decreases with increasing CuO content due to a shift in the active conduction pathway. Above the percolation threshold of CuO, the conduction takes place via the CuO grains that form a continuous network. On the contrary, below the percolation threshold of CuO, solid state diffusion occurs via CeO$_{2-x}$ bridges, which have a high energy barrier for charge transport than CuO bridges. Redox experiments in a TGA at 700 ºC showed that the rate of bulk oxidation increases with increasing CuO content due to a decrease in the activation energy for solid state diffusion, indicating that the ionic conduction of oxygen is the rate determining step.
Chapter 7

Development of MgAl$_2$O$_4$-stabilized, Cu-doped, Fe$_2$O$_3$-based oxygen carriers for thermochemical water splitting

7.1 Introduction

Hydrogen is an important feedstock in the chemical industry and may, in view of climate change, become also a more important fuel in the future. However, the currently available technologies for the large scale production of H$_2$, e.g. steam methane reforming and coal gasification, are very energy intensive and release large quantities of CO$_2$ into the atmosphere.$^{131}$ Thus, for H$_2$ to become a major energy carrier, it must be produced in an efficient and ‘sustainable’ manner, i.e. if derived from fossil resources, H$_2$ must be produced in combination with carbon dioxide capture and storage (CCS). In this context, thermochemical water splitting is a promising process to produce high purity H$_2$ (without the need of additional energy intensive H$_2$ purification steps) while simultaneously capturing CO$_2$.\(^{132}\) In the chemical looping-based water splitting cycle studied here, a hydrocarbon fuel is used to reduce an oxygen carrier. The reduced oxygen carrier is subsequently re-oxidized by steam to produce high purity H$_2$. Depending on thermodynamics and process configurations, an additional air oxidation step may be included after steam oxidation, allowing for an additional heat output. Iron oxide (Fe$_2$O$_3$) is a very attractive candidate for thermochemical water splitting owing to its low cost, wide availability, minimal environmental impact and high equilibrium partial pressure of H$_2$.\(^{133}\) The iron oxide-based thermochemical water splitting cycle was originally referred to as the ‘steam-iron process’.\(^{134}\) A schematic diagram of the iron oxide-mediated water splitting process, using methane (CH$_4$) as a fuel, is shown in Figure 7.1.
Figure 7.1. Schematic diagram of the steam-iron process.

Depending on the ratio of CH$_4$ to Fe$_2$O$_3$, the reduction of Fe$_2$O$_3$ with CH$_4$ occurs via:

$$\text{CH}_4 + 3\text{Fe}_2\text{O}_3 \rightarrow \text{CO} + 2\text{H}_2 + 2\text{Fe}_3\text{O}_4 \quad \Delta H_{1173 \, \text{K}} = 215.5 \, \text{kJ/mol} \quad (7.1a)$$

$$\text{CH}_4 + \text{Fe}_3\text{O}_4 \rightarrow \text{CO} + 2\text{H}_2 + 3\text{FeO} \quad \Delta H_{1173 \, \text{K}} = 262.8 \, \text{kJ/mol} \quad (7.1b)$$

$$\text{CH}_4 + \text{FeO} \rightarrow \text{CO} + 2\text{H}_2 + \text{Fe} \quad \Delta H_{1173 \, \text{K}} = 250.9 \, \text{kJ/mol} \quad (7.1c)$$

or

$$\text{CH}_4 + 12\text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{Fe}_3\text{O}_4 \quad \Delta H_{1173 \, \text{K}} = 145.1 \, \text{kJ/mol} \quad (7.2a)$$

$$\text{CH}_4 + 4\text{Fe}_3\text{O}_4 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 12\text{FeO} \quad \Delta H_{1173 \, \text{K}} = 334.3 \, \text{kJ/mol} \quad (7.2b)$$

$$\text{CH}_4 + 4\text{FeO} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{Fe} \quad \Delta H_{1173 \, \text{K}} = 286.6 \, \text{kJ/mol} \quad (7.2c)$$

Subsequently, Fe is re-oxidized using steam to produce a pure stream of H$_2$:

$$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 4\text{H}_2 \quad \Delta H_{1173 \, \text{K}} = -103.1 \, \text{kJ/mol} \quad (7.3)$$

To close the cycle, Fe$_3$O$_4$ is oxidized back to Fe$_2$O$_3$ using air, *viz.*:
\[
4\text{Fe}_2\text{O}_3 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3 \quad \Delta H_{1173\text{ K}} = -237.0 \text{ kJ/mol} \quad (7.4)
\]

Addition of reactions 7.1b, 7.1c and 7.3 yields the conventional steam reformation of CH\(_4\):
\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{1173\text{ K}} = 228.1 \text{ kJ/mol} \quad (7.5)
\]

However, unlike in conventional steam reforming, in the iron oxide-mediated process described above, a pure stream of H\(_2\) is produced inherently. Moreover, the synthesis gas produced during the partial oxidation of CH\(_4\) (reaction 7.1) has a H\(_2\) to CO ratio of 2:1 and is, thus, suitable for methanol or Fischer-Tropsch synthesis.\(^{135}\) Compared to steam methane reforming, the exergetic efficiency of the iron oxide mediated water splitting process is promising;\(^{136}\) however, the poor cyclability of pure, \textit{i.e.} unsupported, Fe\(_2\)O\(_3\) is currently a major drawback. It has been found that if reduced down to metallic Fe, unsupported Fe\(_2\)O\(_3\) deactivates after only a few cycles, probably due to thermal sintering.\(^{27}\) To reduce its tendency for thermal sintering, Fe\(_2\)O\(_3\) is commonly stabilized with a high Tammann temperature support, \textit{e.g.} Al\(_2\)O\(_3\), ZrO\(_2\), TiO\(_2\) or MgAl\(_2\)O\(_4\).\(^{16}\) Previous studies of the iron oxide-mediated water splitting process have largely focused on using CO or synthesis gas (CO + H\(_2\)) as the reducing agents.\(^{48, 75, 137-140}\) The preference for CO (or synthesis gas) can be explained by the fact that carbon deposition \textit{via} the Boudouard reaction (2CO \rightarrow C + CO\(_2\)) is thermodynamically limited at temperatures above 800 °C (\(K_p = \sim 0.15\) at 800 °C), whereas Fe catalyzes CH\(_4\) decomposition,\(^{141}\) \textit{viz.}:
\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H_{1173\text{ K}} = 58.5 \text{ kJ/mol} \quad (7.6)
\]

Moreover, the oxygen carriers developed so far have shown a poor reactivity with CH\(_4\) when compared to H\(_2\) or CO.\(^{142, 143}\) However, it should be noted that CO and synthesis gas are not primary fuels. Therefore, it is important to develop Fe\(_2\)O\(_3\)-based materials that have a high reactivity with CH\(_4\) and, at the same time, a low propensity for coke formation when using inexpensive CH\(_4\) as a fuel.

One approach to diminish CH\(_4\) decomposition related carbon deposition is to limit the reduction of Fe\(_2\)O\(_3\) to FeO, since FeO catalyzes only poorly reaction 7.6 when compared to metallic Fe.\(^{144}\) However, this process modification reduces largely the yield of H\(_2\) expressed as mol H\(_2\)/gOC, since the H\(_2\) yield for FeO oxidation is three times lower than for Fe oxidation. An alternative approach to suppress the formation of carbon during CH\(_4\) oxidation while at the same time ensuring a high H\(_2\) yield is the doping of Fe\(_2\)O\(_3\) with a transition metal that is inactive for the dissociation of CH\(_4\), \textit{e.g.} Cu, Pt or Pd.
In this context, Cu is an attractive candidate because of its low cost and high activation energy for the dissociative chemisorption of CH\(_4\) (compared to Pt and Pd).\(^{145}\) However, the main disadvantage of doping Fe\(_2\)O\(_3\) with Cu is the possible formation of low Tammann temperature solid solutions, e.g. CuFe\(_2\)O\(_4\) (Tammann temperature of only \(~400\, ^\circ\text{C}\)).\(^{146}\) So far only Kang et al.\(^{147}\) have studied the redox characteristics of co-precipitated CuFe\(_2\)O\(_4\); however, only five redox cycles were performed (CH\(_4\) reduction at 900 \(^\circ\text{C}\) for 50 min followed by steam oxidation at 800 \(^\circ\text{C}\) for 120 min). It was reported that compared to unsupported Fe\(_2\)O\(_4\), CuFe\(_2\)O\(_4\) exhibited fast reduction kinetics, a low carbon deposition and high CO selectivity. Nonetheless, large fluctuations in the CH\(_4\) conversion (33–55 mol. %) and H\(_2\) yield (6.7–11.3 mmol/g\(_{\text{oC}}\)) were observed over the 5 cycles tested (probably due to sintering). To stabilize the H\(_2\) yield, Kang et al.\(^{147}\) supported CuFe\(_2\)O\(_4\) on ZrO\(_2\) or CeO\(_2\). However, this approach resulted in a reduction in the quantity of the active phase (CuFe\(_2\)O\(_4\)) to only 20 wt. % CuFe\(_2\)O\(_4\), a value that is arguably too small for practical applications. Nonetheless, supported CuFe\(_2\)O\(_4\) showed a higher CH\(_4\) conversion when compared to pure CuFe\(_2\)O\(_4\). However, somewhat surprisingly the oxidation kinetics of the new oxygen carrier were reduced substantially, \textit{viz.} 80 min were required to fully re-oxidize ZrO\(_2\) or CeO\(_2\) supported CuFe\(_2\)O\(_4\) (1 g oxygen carrier and gas space velocity \(~4\, \text{min}^{-1}\)). In addition, the very low loading of CuFe\(_2\)O\(_4\) in the material reduced the overall H\(_2\) yield to only 2 mmol/g\(_{\text{oC}}\).

In this Chapter, the potential of Cu-promoted, Fe\(_2\)O\(_3\)-based oxygen carriers for iron oxide-mediated water splitting is demonstrated. CuO-Fe\(_2\)O\(_3\) was effectively stabilized on MgAl\(_2\)O\(_4\) using only 10 wt. % support, thus, ensuring high H\(_2\) yields. The cyclic redox stability and water splitting characteristics were determined and interpreted in light of the morphological and phase characteristics of the material. In order to understand the role of Cu in inhibiting carbon deposition, the reduced oxygen carriers were studied using extended X-ray absorption fine structure spectroscopy and energy dispersive X-ray spectroscopy. The materials developed here show very little coke deposition while at the same time maintaining high and stable H\(_2\) yields over many redox cycles.

**7.2 Experimental**

**7.2.1 Oxygen carrier synthesis**

MgAl\(_2\)O\(_4\)-stabilized, Cu-modified, Fe\(_2\)O\(_3\)-based oxygen carriers were synthesized \textit{via} a modified co-precipitation technique originally reported by He \textit{et al.}\(^{123}\) The quantity of
Fe$_2$O$_3$ in the synthesized oxygen carriers was between 70–75 wt. %, while the Cu content (after reduction of CuO) was varied from 0–25 wt. %, the balance being MgAl$_2$O$_4$. In a typical synthesis, first appropriate amounts of Fe(NO$_3$)$_3$·9H$_2$O, Cu(NO$_3$)$_2$·2.5H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were dissolved in 400 mL of deionized water (15 MΩ·cm at 25 ºC). The molar ratio of Mg$^{2+}$ to Al$^{3+}$ was fixed to 1:2, while the total moles of cations were fixed to 0.3. Subsequently, 400 mL of an aqueous solution containing 24 g NaOH and 6 g Na$_2$CO$_3$ was added dropwise to the nitrate solution under continuous stirring. The pH of the resulting slurry was adjusted to ~8.5 using NaOH. The mixture was kept at 80 ºC for 15 h under reflux. The resulting precipitate was filtered and washed several times with deionized water. The cake of the washed precipitate was dried in an oven at 70 ºC for 24 h and subsequently calcined in a muffle furnace at 900 ºC for 2 h using a temperature ramp of 5 ºC/min. The calcined oxygen carriers were crushed and sieved into the size range 300–425 µm. The following nomenclature is used to describe the composition of the oxygen carriers: the symbols Fe, Cu and MgAl are followed by the weight percentage of Fe$_2$O$_3$, Cu and MgAl$_2$O$_4$ in the oxygen carrier, respectively. For example, Fe71Cu02MgAl27 is an oxygen carrier that contains 71 wt. %, 2 wt. % and 27 wt. % of Fe$_2$O$_3$, Cu (after reduction of CuO) and MgAl$_2$O$_4$, respectively.

7.2.2 Oxygen carrier characterization

The crystallinity and chemical composition of the freshly calcined and cycled oxygen carriers was determined using a Bruker AXS D8 Advance X-ray diffractometer mounted with a Lynx eye super speed detector. The diffractometer was operated at 40 kV and 40 mA using Cu K$_\alpha$ radiation ($\lambda = 1.5418$ nm). Each sample was scanned within the range of $2\theta = 20–80^\circ$ using a step size of 0.0275° per second. X-ray diffractograms were further refined using the General Structure Analysis System (GSAS). EXAFS spectroscopy was performed at the Swiss-Norwegian beamline (SNBL, BM01B) of the European Synchrotron Radiation Facility (ESRF) to study the local structure of Fe and Cu in the reduced oxygen carriers. The oxygen carriers were mixed with cellulose (ratio 1:8) and pelletized. The pellets were scanned in transmission mode to acquire Fe and Cu K-edge EXAFS data. The acquired data were subsequently processed using the IFEFFIT package.

N$_2$ adsorption and desorption isotherms of the oxygen carriers were measured at -196 ºC (Quantachrome NOVA 4000e analyzer). Each sample was degassed for 3 h at 300 ºC prior to the measurement. The surface area and pore volume were calculated using,
respectively, the Brunauer et al.\textsuperscript{62} and Barrett et al.\textsuperscript{63} models. Scanning electron microscopy (Zeiss LEO 1530 FEG) was applied to characterize the surface morphology of the fresh and cycled oxygen carriers. The average grain size was determined from electron micrographs using the ImageJ software package.\textsuperscript{150} The average grain size (and error bar) reported is based on the analysis of 50 individual grains. The elemental composition of the surface was mapped using EDX spectroscopy.

\textsuperscript{CH4}-TPR was performed in a Mettler Toledo TGA (TGA/DSC 1). In a typical experiment, a small amount (~30 mg) of the oxygen carrier was heated from room temperature to 1000 °C at a rate of 10 °C/min under a flow of 10 vol. % CH\textsubscript{4} in N\textsubscript{2} (50 mL/min) and kept at 1000 °C for 30 min. In all experiments, a constant N\textsubscript{2} flow of 25 mL/min was used as purge flow over the microbalance. Raman spectroscopy (Thermo Scientific DXR Raman microscope) was performed to characterize the carbon deposited on the reduced oxygen carriers. Raman spectra were collected by exciting the samples with 10 % power of a 780 nm laser (24 mW total power) for 10 s at 1 cm\textsuperscript{-1} spectral resolution.

\textbf{7.2.3 Fixed bed measurements}

The redox performance of the synthesized oxygen carriers was evaluated in a fixed bed reactor at 900 °C. A schematic diagram of the experimental set-up is given in Appendix A1.3. In a typical experiment, the oxygen carrier was reduced with 10 vol. % CH\textsubscript{4} in N\textsubscript{2} (1.5 L/min at 25 °C and 1 bar). The reduced oxygen carrier was subsequently re-oxidized with 15 vol. % steam in N\textsubscript{2}. The flow rate of the steam/N\textsubscript{2} mixture was 2.83 L/min (at 200 °C and 1 bar). To close the cycle, the oxygen carrier was oxidized back to Fe\textsubscript{2}O\textsubscript{3} with 5 vol. % O\textsubscript{2} in N\textsubscript{2} using a flow rate of 1.97 L/min (at 25 °C and 1 bar). The duration of the CH\textsubscript{4} reduction, steam oxidation and air oxidation segments was fixed to 15 min, 8 min and 5 min, respectively. The reactor was purged for 1 min with N\textsubscript{2} (1.5 L/min) after every segment. In total 15 cycles were performed. The moles of H\textsubscript{2} produced during steam oxidation were calculated by integrating the molar flow rate of H\textsubscript{2} produced with respect to time.
7.3 Results

7.3.1 Characterization of the freshly calcined oxygen carriers

The composition of the freshly calcined oxygen carriers was determined using XRD (Figure 7.2). Hematite (Fe$_2$O$_3$) and MgAl$_2$O$_4$ were identified in fresh Fe70MgAl30. Rietveld refinement of the XRD data of Fe70MgAl30 gave ~71.5 wt. % Fe$_2$O$_3$ which is in good agreement with the theoretical value of 70 wt. %. MgAl$_2$O$_4$-stabilized, Cu-modified, Fe$_2$O$_3$-based oxygen carriers showed the formation of Fe$_2$O$_3$, CuFe$_2$O$_4$ and MgAl$_2$O$_4$. The X-ray diffractogram of fresh Fe71Cu02MgAl27 contained peaks due to Fe$_2$O$_3$ and MgAl$_2$O$_4$ only, probably because the quantity of Cu$^{2+}$ phases (CuO or CuFe$_2$O$_4$) was below the detection limit of the equipment. Rietveld refinement of the XRD data of Fe71Cu02MgAl27 yielded 70.9 wt. % Fe$_2$O$_3$ and 29.1 wt. % MgAl$_2$O$_4$, again in good agreement with the theoretically expected composition (71.0 wt. % Fe$_2$O$_3$, 2.0 wt. % Cu and 27.0 wt. % MgAl$_2$O$_4$). The composition of Fe71Cu08MgAl21 was determined (Rietveld...
refinement) as 53.7 wt. % Fe₂O₃, 27.0 wt. % CuFe₂O₄ and 19.3 wt. % MgAl₂O₄. Assuming that all the CuO in Fe₇₁Cu₀₈MgAl₂₁ forms CuFe₂O₄, ~30 wt. % CuFe₂O₄ would be expected theoretically in the calcined material. Interestingly, MgAl₂O₄ could not be observed in the diffractogram of Fe₇₃Cu₁₇MgAl₁₀, indicating its presence in an amorphous form. The predicted composition of Fe₇₃Cu₁₇MgAl₁₀ (35.3 wt. % Fe₂O₃ and 64.7 wt. % CuFe₂O₄) was again in good agreement with its theoretical composition (30.0 wt. % Fe₂O₃, 60.0 wt. % CuFe₂O₄ and 10.0 wt. % MgAl₂O₄, assuming the full solution of CuO into Fe₂O₃ forming CuFe₂O₄). Finally, only Bragg reflections corresponding to CuFe₂O₄ were identified in the diffractogram of fresh Fe₇₅Cu₂₅. Assuming a full solution of CuO into Fe₂O₃, 90.2 wt. % CuFe₂O₄ and 9.8 wt. % Fe₂O₃ would be expected for Fe₇₅Cu₂₅. Thus, the XRD measurements indicate that in Fe₇₅Cu₂₅, Fe₂O₃ may be present in an amorphous form.

Figure 7.3 shows scanning electron micrographs of pure, i.e. unsupported Fe₂O₃, pure CuO and freshly calcined oxygen carriers. The surfaces of unsupported Fe₂O₃ and CuO are comprised of micrometer-sized polyhedrons (Figure 7.3(g) shows some sintering for unsupported CuO). On the other hand, the bimetallic oxygen carriers reveal different surface morphologies compared to unsupported Fe₂O₃ and CuO. The surfaces of Fe₇₀MgAl₃₀ and Fe₇₁Cu₀₂MgAl₂₇ are comprised of nanometer-sized grains, as seen in Figures 7.3(a) and (b), respectively. The average size of the grains was determined as 88 ± 14 nm and 124 ± 16 nm for, respectively, Fe₇₀MgAl₃₀ and Fe₇₁Cu₀₂MgAl₂₇. The surfaces of Fe₇₁Cu₀₈MgAl₂₁ and Fe₇₃Cu₁₇MgAl₁₀ showed some sintering and were, only in parts, comprised of small grains. The sintering tendency of the bimetallic oxygen carriers (based on a visual inspection of the electron micrographs) was found to increase with increasing CuO content and can be explained by the low Tammann temperature of CuFe₂O₄ of only ~400 °C. Indeed, Figure 7.3(e) shows that Fe₇₅Cu₂₅ (almost pure CuFe₂O₄) has a very smooth surface texture possibly due to severe thermal sintering during calcination.
Figure 7.3. Scanning electron micrographs of the calcined oxygen carriers: (a) Fe70MgAl30, (b) Fe71Cu02MgAl27, (c) Fe71Cu08MgAl21, (d) Fe73Cu17MgAl10, (e) Fe75Cu25, (f) pure, i.e. unsupported Fe$_2$O$_3$ and (g) pure CuO. The materials were calcined at 900 ºC for 2 h.
The BET surface area and BJH pore volume of the calcined oxygen carriers obtained, respectively, from N\textsubscript{2} adsorption and desorption isotherms are summarized in Table 7.1. As expected from the electron micrographs, Fe\textsubscript{70}MgAl\textsubscript{30} possessed the highest surface area and pore volume of all oxygen carriers synthesized. For the remaining oxygen carriers, a significant reduction in surface area and pore volume was observed for increasing Cu contents, most likely due to thermal sintering during calcination, as visualized in the electron micrographs shown in Figure 7.3.

<table>
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<tr>
<th>Material</th>
<th>BET surface area [m\textsuperscript{2}/g]</th>
<th>BJH pore volume [cm\textsuperscript{3}/g]</th>
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</tr>
<tr>
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<td>0.05</td>
</tr>
<tr>
<td>Fe\textsubscript{71}Cu\textsubscript{08}MgAl\textsubscript{21}</td>
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<td>0.02</td>
</tr>
<tr>
<td>Fe\textsubscript{73}Cu\textsubscript{17}MgAl\textsubscript{10}</td>
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<td>Fe\textsubscript{75}Cu\textsubscript{25}</td>
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<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

7.3.2 CH\textsubscript{4}-temperature programmed reduction

CH\textsubscript{4}-TPR was performed to compare the reactivity of unsupported Fe\textsubscript{2}O\textsubscript{3}, CuO, CuFe\textsubscript{2}O\textsubscript{4} and the synthesized oxygen carries with CH\textsubscript{4} (Figure 7.4). The onset of reduction was defined as the temperature at which the oxygen carrier had lost 2 % of the total weight loss. The reduction was considered to be completed once 98 % of the total weight loss had been reached. Figure 7.4 shows that pure CuO was reduced in a single step in the temperature range 480–900 °C. On the other hand, the reduction of pure Fe\textsubscript{2}O\textsubscript{3} and CuFe\textsubscript{2}O\textsubscript{4} started at ~650 °C and ~750 °C, respectively, and did not reach completion during the measurement time. Compared to unsupported Fe\textsubscript{2}O\textsubscript{3}, the reduction of MgAl\textsubscript{2}O\textsubscript{4}-supported Fe\textsubscript{2}O\textsubscript{3} (Fe\textsubscript{70}MgAl\textsubscript{30}) started at a considerably lower temperature, viz. at ~460 °C. For Fe\textsubscript{70}MgAl\textsubscript{30}, a three step reduction mechanism was identified in the CH\textsubscript{4}-TPR profile. The weight loss observed in the first step (temperature range 460–580 °C) agrees with the Fe\textsubscript{2}O\textsubscript{3}–Fe\textsubscript{3}O\textsubscript{4} transition. Similarly, the weight losses recorded during the second and third steps correspond to the Fe\textsubscript{3}O\textsubscript{4}–FeO and FeO–Fe transitions, respectively. The reduction of Fe\textsubscript{3}O\textsubscript{4} and FeO started at ~620 °C and ~800 °C, respectively. The increase in sample weight during the holding time (1000 °C) was due to carbon deposition via CH\textsubscript{4} decomposition.
The Raman spectrum of reduced Fe70MgAl30 also confirmed the deposition of graphite on its surface, see Figure 7.5(b). The Raman shift at 1582 cm\(^{-1}\) (G band) corresponds to the sp\(^2\) carbon networks of graphite. The so-called D and D′ bands (at 1310 cm\(^{-1}\) and 1620 cm\(^{-1}\), respectively) are the defect induced Raman features of graphite. The diffractogram of reduced Fe70MgAl30 (Figure 7.5(a)) revealed the presence of Fe, MgAl\(_2\)O\(_4\) and Fe\(_3\)C.

![Graph showing normalized weight loss vs temperature for different oxygen carriers](image)

**Figure 7.4.** CH\(_4\)-TPR profiles of the synthesized oxygen carriers: (− −) pure Fe\(_2\)O\(_3\), (⋯⋯) pure CuO, (− · −) commercial CuFe\(_2\)O\(_4\), (−) Fe70MgAl30, (−−) Fe71Cu02MgAl27, (−−) Fe71Cu08MgAl21, (−−) Fe73Cu17MgAl10 and (−−) Fe75Cu25.

The reduction of Fe71Cu02MgAl27 and Fe71Cu08MgAl21 also occurred in three steps. The weight loss in the first step is in agreement with the CuO–Cu and Fe\(_2\)O\(_3\)–Fe\(_3\)O\(_4\)
transitions. The weight losses recorded in the second and third steps match well the theoretically predicted weight losses for the Fe$_3$O$_4$–FeO and FeO–Fe transitions. For Fe$_{71}$Cu$_{02}$MgAl$_{27}$, the first, second and third reduction steps started at ~480 ºC, ~690 ºC and ~800 ºC, respectively. Interestingly, the weight increase of Fe$_{71}$Cu$_{02}$MgAl$_{27}$ due to carbon deposition was appreciably lower compared to Fe$_{70}$MgAl$_{30}$. Indeed, peaks due to Fe$_3$C could not be observed in the diffractogram of reduced (and further exposed to CH$_4$) Fe$_{71}$Cu$_{08}$MgAl$_{21}$ (Figure 7.5(a)), indicating that the presence of Cu inhibited notably carbon deposition. The reduction of Fe$_{71}$Cu$_{08}$MgAl$_{21}$ started at ~510 ºC, with the second and third reduction steps occurring at ~710 ºC and ~820 ºC, respectively. For Fe$_{71}$Cu$_{08}$MgAl$_{21}$, the tendency for carbon deposition was reduced further when compared to Fe$_{70}$MgAl$_{30}$ and Fe$_{71}$Cu$_{02}$MgAl$_{27}$. Only Fe and Cu were identified in the diffractogram of reduced (and further exposed to methane) Fe$_{71}$Cu$_{08}$MgAl$_{21}$.

The reduction of Fe$_{73}$Cu$_{17}$MgAl$_{10}$ was found to occur in four steps. The weight losses recorded for the first, second, third and fourth step correspond to the CuFe$_2$O$_4$–Cu + Fe$_2$O$_3$, Fe$_2$O$_3$–Fe$_3$O$_4$, Fe$_3$O$_4$–FeO and FeO–Fe transitions, respectively. The reduction of CuFe$_2$O$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO in Fe$_{73}$Cu$_{17}$MgAl$_{10}$ started at ~580 ºC, ~660 ºC, ~760 ºC and ~890 ºC, respectively. Interestingly, no increase in sample weight and, thus, no carbon deposition was observed for Fe$_{73}$Cu$_{17}$MgAl$_{10}$. The diffractogram of the reduced Fe$_{73}$Cu$_{17}$MgAl$_{10}$ showed peaks due to Fe and Cu only. The CH$_4$-TPR profile of Fe$_{75}$Cu$_{25}$ revealed a single reduction step in the temperature range 650–930 ºC. The weight loss recorded is in agreement with the reductions of CuFe$_2$O$_4$ to Cu + Fe$_2$O$_3$ and Fe$_2$O$_3$ to FeO. The diffractogram of reduced Fe$_{75}$Cu$_{25}$ showed peaks due to FeO, Fe and Cu, indicative of a very slow reduction of FeO to Fe in Fe$_{75}$Cu$_{25}$ (as confirmed in Figure 7.4). No carbon deposition was observed for the reference material Fe$_{75}$Cu$_{25}$ as it was not fully reduced to metallic Fe at the end of the experiment (Figure 7.5(b)).
Figure 7.5. (a) X-ray diffractograms of the reduced oxygen carriers: (—) Fe\textsubscript{70}Mg\textsubscript{30}, (—) Fe\textsubscript{71}Cu\textsubscript{2}Mg\textsubscript{27}, (—) Fe\textsubscript{71}Cu\textsubscript{8}Mg\textsubscript{21}, (—) Fe\textsubscript{73}Cu\textsubscript{17}Mg\textsubscript{10} and (—) Fe\textsubscript{75}Cu\textsubscript{25}. The following compounds were identified: (■) Fe, (▲) Fe\textsubscript{3}C, (♦) Mg\textsubscript{2}Al\textsubscript{4}O\textsubscript{4}, (●) Cu and (●) FeO. (b) Raman spectra of reduced (—) Fe\textsubscript{70}Mg\textsubscript{30} and (—) Fe\textsubscript{75}Cu\textsubscript{25}. 
7.3.3 Redox performance of the synthesized oxygen carriers

The cyclic redox performance of the synthesized oxygen carriers was assessed in a fixed bed reactor at 900 °C (reduction in 10 vol. % CH₄ in N₂). The yield of H₂ during steam oxidation is plotted as a function of cycle number in Figure 7.6. Figures 7.7(a) and (b) plot, respectively, the molar ratio of H₂ to CO in the synthesis gas and the moles of COₓ produced during the oxidation of CH₄ as a function of cycle number. It can be observed that the H₂ yield of Fe70MgAl30 was ~3.5 times higher than the theoretically expected value (11.6 mmol H₂/g_oc, assuming a full reduction to Fe) with some fluctuations during the first ten cycles. For Fe71Cu02MgAl27, Fe71Cu08MgAl21 and Fe73Cu17MgAl10 a stable H₂ yield of, respectively, ~16.2 mmol H₂/g_oc, ~14.2 mmol H₂/g_oc and ~13.6 mmol H₂/g_oc was obtained over the 15 redox cycles tested. Finally, the reference material Fe75Cu25 showed a stable, but low H₂ yield of ~4.2 mmol H₂/g_oc, which is only ~36 % of the theoretically expected value.

![Figure 7.6](image)

**Figure 7.6.** H₂ yield during re-oxidation using 15 vol. % steam in N₂. The experiments were performed in a fixed bed at 900 °C and the duration of the steam oxidation reaction was fixed to 8 min: (●) Fe70MgAl30, (×) Fe71Cu02MgAl27, (■) Fe71Cu08MgAl21, (♦) Fe73Cu17MgAl10 and (▲) Fe75Cu25. The dashed line corresponds to the theoretical H₂ yield of 11.6 mmol H₂/g_oc for an oxygen carrier containing 70 wt. % Fe₂O₃.
Turning now to the production of a synthesis gas during the reduction of the oxygen carriers with methane, Figure 7.7(a) shows that the H$_2$ to CO ratio for Fe70MgAl30 fluctuated somewhat during the first 10 cycles. From the eleventh cycle onwards, the H$_2$ to CO ratio stabilized at ~9:1. On the other hand, Cu-modified oxygen carriers showed
a significantly lower H$_2$ to CO ratio. For Fe71Cu03MgAl27, the H$_2$ to CO ratio was ~6:1 in the first cycle which decreased to ~5:1 in the fifteenth cycle. In case of Fe71Cu08MgAl21 and Fe73Cu17MgAl10 the H$_2$ to CO ratio remained stable at ~3:1 over repeated redox cycles. Finally, for the reference material Fe75Cu25 a synthesis gas with a H$_2$ to CO ratio of ~4:1 was obtained in the first cycle. However, the H$_2$ to CO ratio gradually increased, reaching ~5:1 in the fifteenth cycle. Among the synthesized oxygen carriers, Fe75Cu25 possessed the lowest CO yield of only ~1.2 mmol CO/g$_{OC}$, see Figure 7.7(b). On the other hand, the CO yield of the MgAl$_2$O$_4$-stabilized oxygen carriers was 6–7 times higher than that of unsupported Fe75Cu25. It is also worth noting that the CO$_2$ yield of all oxygen carriers tested was ~1.5 mmol CO$_2$/g$_{OC}$, independent of whether Fe$_2$O$_3$ was supported or promoted with Cu.

### 7.3.4 Carbon deposition

![Figure 7.8](image)

**Figure 7.8.** Carbon deposition during the reduction of the oxygen carriers in CH$_4$. The experiments were performed at 900 °C in a fixed bed: (●) Fe70MgAl30, (∗) Fe71Cu02MgAl27, (■) Fe71Cu08MgAl21, (♦) Fe73Cu17MgAl10 and (▲) Fe75Cu25.

Carbon deposition via CH$_4$ decomposition during the reduction step decreases the purity of the H$_2$ produced during steam oxidation owing to the simultaneous formation of CO$_x$. Figure 7.8 plots the moles of carbon deposited during the CH$_4$ reduction step as a function of cycle number. The quantity of carbon deposited was calculated from the moles of CO$_x$ produced during re-oxidation. The activity for CH$_4$ decomposition over the 15 redox cycles tested decreased in the following order: Fe70MgAl30 > Fe71Cu02MgAl27 >
Fe71Cu08MgAl21 > Fe73Cu17MgAl10 > Fe75Cu25. The average quantity of carbon deposited on the oxygen carriers over 15 redox cycles was 28.3 mmol/g\(_{\text{OC}}\), 3.7 mmol/g\(_{\text{OC}}\), 2.7 mmol/g\(_{\text{OC}}\), 1.8 mmol/g\(_{\text{OC}}\) and 0.4 mmol/g\(_{\text{OC}}\) for Fe70MgAl30, Fe71Cu02MgAl27, Fe71Cu08MgAl21, Fe73Cu17MgAl10 and Fe75Cu25, respectively.

**Figure 7.9.** (a) Fe K-edge EXAFS functions (\(k^2\)-weighted) of (—) Fe foil, (—) reduced Fe70MgAl30 and (—) reduced Fe73Cu17MgAl10. (b) Cu K-edge EXAFS functions (\(k^2\)-weighted) of (—) Cu foil and (—) reduced Fe73Cu17MgAl10.

To understand better the inhibiting effect of Cu for carbon deposition, reduced Fe70MgAl30 and Fe73Cu17MgAl10 were studied using EXAFS spectroscopy. The acquired Fe and Cu K-edge EXAFS functions of the reduced materials are plotted in Figure 7.9(a)
and (b), respectively. The EXAFS functions of the reference Fe and Cu foils are also provided in Figure 7.9. The Fe K-edge EXAFS functions ($k^2$-weighted) of both oxygen carriers examined are similar to the reference Fe foil. Fitting of the first shell around the central Fe atom confirms that the experimentally determined Fe-Fe distances in the reduced oxygen carriers (Table 7.2) are similar to the Fe-Fe distances in the reference Fe foil. A slightly higher Debye-Waller factor ($\sigma^2$), which indicates disorder, was determined for the reduced oxygen carriers when compared to the reference Fe foil. Similarly, the $k^2$-weighted Cu K-edge EXAFS function of the reduced Fe73Cu17MgAl10 resembles well the EXAFS function of the reference Cu foil. Fitting of the first shell around the central Cu atom yielded similar Cu-Cu distances as in the reference Cu foil (Table 7.3). The Debye-Waller factor of reduced Fe73Cu17MgAl10 was again higher when compared to the Cu foil. Importantly, the acquired Fe and Cu K-edge EXAFS functions of the reduced oxygen carriers confirmed that Fe and Cu did not form an alloy. The surface of the reduced Fe73Cu17MgAl10 was also probed via EDX spectroscopy. The Fe L-edge EDX spectrum of the reduced Fe73Cu17MgAl10 (Figure 7.10(b)) indicates that Fe is present on the entire surface of the reduced material. However, the Cu L-edge EDX spectrum (Figures 7.10(c)) and the contrast in Figure 7.10(b) suggest that Cu covers Fe only partially on the surface of reduced Fe73Cu17MgAl10.

Table 7.2. Structural parameters for the first Fe-Fe shell in the reference Fe foil and reduced oxygen carriers, as determined by refining the theoretical EXAFS functions.

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<td>Fe73Cu17MgAl10</td>
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<td>6.0</td>
<td>2.47 ± 0.01</td>
<td>2.83 ± 0.01</td>
<td>0.0074 ± 0.0003</td>
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$N$ = coordination number, fixed; $R$ = Fe-Fe distance; $\sigma^2$ = EXAFS Debye-Waller factor; R-factor indicates the normalized sum of residuals.
Table 7.3. Structural parameters for the first Cu-Cu shell in the reference Cu foil and reduced Fe73Cu17MgAl10, as determined by refining the theoretical EXAFS functions.

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<th>σ²</th>
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<td>1.90</td>
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N = coordination number, fixed; R = Fe-Fe distance; σ² = EXAFS Debye-Waller factor; R-factor indicates the normalized sum of residuals.

Figure 7.10. (a) Scanning electron micrograph of the reduced Fe73Cu17MgAl10, (b) Fe L-edge, (c) Cu L-edge and (d) Fe and Cu L-edge EDX spectra.

7.3.5 Characterization of the cycled oxygen carriers

X-ray diffractograms, scanning electron micrographs and N₂-physisorption isotherms of the cycled oxygen carriers (oxidized form) were acquired to probe compositional and morphological changes over repeated redox cycles. Figure 7.11 shows that compared to the freshly calcined materials, additional crystalline phases appeared in the cycled samples.
For example, magnesium aluminum iron oxide (MgAl$_{0.6}$Fe$_{1.4}$O$_4$) was identified in the diffractograms of cycled Fe70MgAl30, Fe71Cu02MgAl27 and Fe71Cu08MgAl21. Cycled Fe73Cu17MgAl10 was found to be comprised mainly of CuFe$_2$O$_4$ and Fe$_2$O$_3$, however, weak Bragg reflections due to delafossite, CuFeO$_2$, were also identified. Intriguingly, MgAl$_2$O$_4$ could not be observed in cycled Fe73Cu17MgAl10. Finally, cycled Fe75Cu25 contained CuFe$_2$O$_4$, CuFeO$_2$ and Fe$_2$O$_3$.

**Figure 7.11.** X-ray diffractograms of the cycled materials: (—) Fe70MgAl30, (—) Fe71Cu02MgAl27, (—) Fe71Cu8MgAl21, (—) Fe73Cu17MgAl10 and (—) Fe75Cu25. The following compounds were identified: (■) Fe$_2$O$_3$, (♦) MgAl$_{0.6}$Fe$_{1.4}$O$_4$, (▲) MgAl$_2$O$_4$, (◊) CuFe$_2$O$_4$ and (●) CuFeO$_2$.

In addition, also the morphology of the materials changed over multiple redox cycles as confirmed by electron microscopy (Figure 7.12) and N$_2$-physisorption (Table 7.4). For example, the electron micrographs of cycled Fe70MgAl30 (Figure 7.12(a)) and Fe71Cu02MgAl27 (Figure 7.12(b)) show that the nanometer-sized grains, originally present in freshly calcined Fe70MgAl30 and Fe71Cu02MgAl27, had sintered, viz. the average grain size of cycled Fe70MgAl30 (135 ± 20 nm) and Fe71Cu02MgAl27 (210 ± 29 nm) increased by a factor of 1.5. This observation is in line with the significantly reduced BET surface area and BJH pore volume of cycled Fe70MgAl30 and Fe71Cu02MgAl27 (Table 7.4).
The surface morphology of cycled Fe71Cu08MgAl21 (Figure 7.12(c)) and Fe73Cu17MgAl10 (Figure 7.12(d)) was also altered during repeated redox cycles. Cycled Fe71Cu08MgAl21 and Fe73Cu17MgAl10 comprised of large grains that were often fused together. The average grain size was 198 ± 54 nm and 172 ± 41 nm for Fe71Cu08MgAl21 and Fe73Cu17MgAl10, respectively. Comparing the data of Tables 7.1 and 7.4, it can be seen that the surface area and pore volume of Fe71Cu08MgAl21 and Fe73Cu17MgAl10 did not change appreciably over 15 redox cycles. Finally, the electron micrograph of cycled Fe75Cu25 (Figure 7.12(e)) shows a surface comprised of well-defined edges and steps. This change in morphology of Fe75Cu25 was accompanied by an increase in surface area (from < 1 m²/g to 3 m²/g).

**Table 7.4. BET surface area and BJH pore volume of the cycled materials.**

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area [m²/g]</th>
<th>BJH pore volume [cm³/g]</th>
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<td>Fe75Cu25</td>
<td>3</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 7.12. Scanning electron micrographs of cycled oxygen carriers (oxidized form): (a) Fe70MgAl30, (b) Fe71Cu02MgAl27, (c) Fe71Cu08MgAl21, (d) Fe73Cu17MgAl10 and (e) Fe75Cu25.

7.4 Discussion

7.4.1 Reduction characteristics of the synthesized oxygen carriers

CH$_4$-TPR measurements of the synthesized oxygen carriers (Figure 7.4) show that supporting Fe$_2$O$_3$ on MgAl$_2$O$_4$ shifts its reduction to considerably lower temperatures (compared to unsupported Fe$_2$O$_3$). With regard to the lower reduction temperature of MgAl$_2$O$_4$-supported Fe$_2$O$_3$, it is conceivable that the MgAl$_2$O$_4$ support influences the reducibility of Fe$_2$O$_3$ by
modifying CH$_4$ chemisorption and charge transport characteristics of the oxygen carrier. Cui et al.$^{151}$ studied the influence of α-Al$_2$O$_3$ and MgAl$_2$O$_4$ supports on the dissociative chemisorption of CH$_4$ on Ni. Using CH$_4$ pulse experiments, Cui et al.$^{151}$ demonstrated that the MgAl$_2$O$_4$ support lowered the activation energy for CH$_4$ dissociation on Ni sites when compared to α-Al$_2$O$_3$-supported and unsupported Ni. The effect of the support on the reduction temperature of Fe$_3$O$_4$ was also studied by Galinsky et al.$^{118}$ who reported that the reduction temperature of La$_{0.8}$Sr$_{0.2}$FeO$_3$-supported Fe$_3$O$_4$ is roughly 250 °C lower than that of TiO$_2$-supported Fe$_3$O$_4$. The high reactivity of La$_{0.8}$Sr$_{0.2}$FeO$_3$-supported Fe$_3$O$_4$ was attributed to a faster solid state O$^{2-}$ and electron/hole transport from the bulk to the particle surface.

On the other hand, the addition of Cu shifts the reduction of Fe$_3$O$_4$ to higher temperatures, viz. the reduction temperature of Fe$_3$O$_4$ increased in the following order: Fe$_{70}$MgAl$_{30}$ < Fe$_{71}$Cu$_{02}$MgAl$_{27}$ ≈ Fe$_{71}$Cu$_{08}$MgAl$_{21}$ ≈ Fe$_{73}$Cu$_{17}$MgAl$_{10}$ < Fe$_{75}$Cu$_{25}$. CH$_4$-TPR profiles of unsupported Fe$_3$O$_4$ and CuFe$_2$O$_4$ showed that CuFe$_2$O$_4$ and Fe$_3$O$_4$ were reduced at ~750 °C and ~650 °C, respectively. The shift of Cu-containing materials to higher reduction temperatures may be explained by the formation of solid solutions in the oxygen carriers.

The CH$_4$-TPR profiles also revealed that metallic Cu formed through the reduction of CuFe$_2$O$_4$, viz.:

$$3\text{CuFe}_2\text{O}_4 + 4\text{CH}_4 \rightarrow 4\text{CO} + 8\text{H}_2 + 3\text{Cu} + 2\text{Fe}_3\text{O}_4$$ (7.7)

decreases slightly the (apparent) rate of reduction of Fe$_3$O$_4$ (to FeO) and FeO (to Fe). These observations are in line with the fact that the activation of CH$_4$ (CH$_{4,s}$ ↔ CH$_{3,s}$ + H$_s$, s = surface) on Fe is exothermic (heat of reaction = -62.8 kJ/mol) but endothermic on Cu (heat of reaction = 123.1 kJ/mol).$^{152}$ As a consequence, the formation of Cu decreases the (apparent) rate of reduction of Fe$_3$O$_4$ and FeO with CH$_4$.

### 7.4.2 Reactivity measurements

The molar H$_2$ to CO ratio of the synthesis gas produced during the reduction of iron oxide was higher than the theoretically expected value of 2:1. The average molar H$_2$ to CO ratio (over 15 redox cycles) increased in the following order: Fe$_{73}$Cu$_{17}$MgAl$_{10}$ (3:1) ≈ Fe$_{71}$Cu$_{08}$MgAl$_{21}$ (3:1) < Fe$_{71}$Cu$_{02}$MgAl$_{27}$ (5:1) ≈ Fe$_{75}$Cu$_{25}$ (5:1) < Fe$_{70}$MgAl$_{30}$ (9:1). Figure 7.7 indicates that all synthesized oxygen carriers show similar CO$_2$ yields during CH$_4$ oxidation. In contrast, the CO yields of all MgAl$_2$O$_4$-stabilized materials were similar and significantly higher than that of unsupported Fe$_{75}$Cu$_{25}$. Thus, the high H$_2$ to CO ratio of
MgAl\(_2\)O\(_4\)-stabilized materials can be explained only by the deposition of carbon during reduction. Previously, Neal et al.\(^{153}\) have observed four regimes during the reduction of Fe\(_2\)O\(_3\)-based oxygen carriers with CH\(_4\), viz. (i) full oxidation of CH\(_4\) to CO\(_2\), (ii) competing full oxidation to CO\(_2\) and partial oxidation to CO, (iii) partial oxidation of CH\(_4\) to CO and (iv) CH\(_4\) decomposition. For MgAl\(_2\)O\(_4\)-supported materials, the reaction between CH\(_4\) and the oxygen carriers synthesized was sufficiently fast to reach regime (iv) within 15 min, resulting in carbon deposition which in turn led to a high H\(_2\) to CO ratio. This is in line with the observation of Galinsky et al.\(^{143}\) who studied the effect of different supports, viz. Ca\(_{0.8}\)Sr\(_{0.2}\)Ti\(_{0.8}\)Ni\(_{0.2}\)O\(_3\), CeO\(_2\) and MgAl\(_2\)O\(_4\), on the methane conversion characteristics of Fe\(_2\)O\(_3\). Galinsky et al.\(^{143}\) found that MgAl\(_2\)O\(_4\) had the highest activity for CH\(_4\) decomposition. Among the materials tested here, Fe\(_{75}\)Cu\(_{25}\) showed the lowest reactivity with CH\(_4\) probably due to the absence of the MgAl\(_2\)O\(_4\) support (see Figure 7.4). As a consequence, the reduction of Fe\(_{75}\)Cu\(_{25}\) was still in regime (ii) after 15 min. Thus, for Fe\(_{75}\)Cu\(_{25}\) the high H\(_2\) to CO ratio is due to a high CO\(_2\) mole fraction (but low CO mole fraction) in the off-gas.

Turning now to the steam oxidation step, the high propensity of Fe\(_{70}\)MgAl\(_{30}\) for coke formation led to a substantial CO\(_x\) contamination of the H\(_2\) produced according to:

\[
C + H_2O \rightarrow CO + H_2 \quad \Delta H_{900\,^\circC} = 169.6 \text{ kJ/mol} \quad (7.8)
\]

\[
C + 2H_2O \rightarrow CO_2 + 2H_2 \quad \Delta H_{900\,^\circC} = 136.9 \text{ kJ/mol} \quad (7.9)
\]

Owing to severe coke deposition, the H\(_2\) yield of Fe\(_{70}\)MgAl\(_{30}\) was 3.5 times higher than the theoretically expected value. For Cu-modified materials, the quantity of carbon deposited decreased with increasing Cu content. For example, for Fe\(_{71}\)Cu\(_{0.2}\)MgAl\(_{27}\) and Fe\(_{71}\)Cu\(_{0.8}\)MgAl\(_{21}\) the H\(_2\) yield was, respectively, only 1.4 times and 1.2 times higher than the theoretically expected value, indicating that Cu significantly reduced coke deposition. Among all the materials developed, only Fe\(_{73}\)Cu\(_{17}\)MgAl\(_{10}\) possessed a stable H\(_2\) yield that was only slightly higher than the theoretically expected value which is indicative of only very little carbon deposition. Finally, the low H\(_2\) yield of only ~32 % of the theoretically expected value for Fe\(_{75}\)Cu\(_{25}\) is due to the incomplete reduction of FeO to Fe with CH\(_4\). The yield of H\(_2\) obtained through the oxidation of FeO is 3 times lower than that obtained from Fe.
7.4.3 Influence of Cu on CH₄ decomposition

![Figure 7.13](image)

Figure 7.13. A schematic representation of carbon deposition on (a) MgAl₂O₄-stabilized Fe₂O₃ and (b) Cu-modified, MgAl₂O₄-stabilized Fe₂O₃.

CH₄-TPR (Figure 7.4) and reactive measurements (Figure 7.8) confirm that the addition of Cu to MgAl₂O₄-stabilized, Fe₂O₃-based oxygen carriers improved appreciably the materials’ resistance to carbon deposition via CH₄ decomposition. The propensity of the oxygen carriers to carbon deposition decreased with increasing Cu content. CH₄-TPR in combination with Raman spectroscopy (Figure 7.5(b)) showed that the decomposition of CH₄ started once Fe₂O₃ was fully reduced to metallic iron. Previous studies of Bengaard et al.¹⁵⁴ and Besenbacher et al.¹⁵⁵ reported that (i) the dissociation of CH₄ molecules (CH₄ₓ → Cₓ + 4Hₓ) on a metal surface and (ii) the nucleation of graphite on steps and edges play a key role in carbon formation. The reaction enthalpy for CH₄ dissociation over Fe is exothermic (-216.9 kJ/mol) but endothermic (251.5 kJ/mol) for Cu.¹⁵² The EXAFS (Figure 7.9) and EDX (Figure 7.10) measurements confirm that in the reduced oxygen carriers Fe and Cu do not form a solid solution, in line with an experimentally determined Fe-Cu equilibrium phase diagram (using thermal analysis and electron microscopy).¹⁵⁶, ¹⁵⁷ Owing to the phase separation of Cu and Fe, a sharp interface on the surface of the reduced oxygen carriers can be expected, as illustrated in Figure 7.13. It can be speculated that the, at least partial, covering of surface Fe with Cu decreases the rate of CH₄ dissociation, which in turn reduces carbon deposition. Further investigation of the surface (e.g. using X-ray photoelectron spectroscopy) is required to conclusively proof the enrichment of Cu on the surface.
Furthermore, the preliminary kinetic data show that the rate of oxidation of Fe with steam is not significantly affected by the presence of Cu. The fact that Fe and Cu occur in separate phases in the reduced state ensures that Cu-promoted Fe₂O₃ maintains the excellent redox characteristic of Fe₂O₃ such as a high H₂ yield and reaction kinetics during the steam oxidation step.

7.5 Conclusions

In this Chapter, it is demonstrated that MgAl₂O₄-stabilized, Cu-modified, Fe₂O₃-based oxygen carriers possess a high and stable H₂ yield over many redox cycles while maintaining a low propensity for coke deposition. CH₄-TPR experiments revealed that the propensity for coke formation decreased with increasing Cu content. Furthermore, Cu shifted the reduction temperatures of Fe₃O₄ and FeO to slightly higher temperatures (using CH₄). At 900 °C (using 10 vol. % CH₄ in N₂) MgAl₂O₄-stabilized Fe₂O₃ produced a synthesis gas with a high H₂ to CO ratio of 9:1 owing to substantial carbon deposition via CH₄ decomposition. However, increasing the Cu content in the oxygen carrier decreased the H₂ to CO ratio (compared to MgAl₂O₄-stabilized Fe₂O₃). On the other hand, unsupported Cu-modified Fe₂O₃ showed low H₂ yields reaching only ~32 % of the theoretically expected value. This was due to the incomplete reduction of FeO to Fe using CH₄. During steam oxidation, MgAl₂O₄-stabilized, Cu-modified, Fe₂O₃-based oxygen carriers exhibited H₂ yields close to the theoretically expected value owing to a low CH₄ decomposition activity of these materials. EXAFS spectroscopy and EDX spectroscopy confirmed that Fe and Cu did not form an alloy in the reduced oxygen carrier. The high resistance to carbon deposition of Cu-modified oxygen carriers was, therefore, attributed to the (partial) coverage of surface Fe with Cu. Owing to their low tendency for coke deposition Cu-modified, MgAl₂O₄-stabilized, Fe₂O₃-based oxygen carriers produced hydrogen with very little COₓ contamination. The oxygen carrier that contained 73 wt. % Fe₂O₃, 17 wt. % Cu and 10 wt. % MgAl₂O₄ was identified as a highly promising material for CH₄-based water splitting cycles for H₂ production.
Chapter 8

Conclusions and outlook

8.1 Conclusions

This dissertation is concerned with the development of CuO-based oxygen carriers for CLC and CLOU. From a thermodynamic point of view, CuO is arguably the most promising oxygen carrier material owing to its exothermic redox reactions and high oxygen carrying capacity under both CLC and CLOU conditions. However, the low Tammann temperature of CuO requires the development of efficient strategies to stabilize its structure over multiple redox cycles. An important facet of this work was to examine the influence of the materials structure, e.g. local atomic disorder and conductivity, on the redox characteristics of the synthesized materials. To achieve a homogenous mixing between the active phase and the support, a co-precipitation technique was developed (Chapter 2) to synthesize Al₂O₃-stabilized CuO. It was found that the pH value at which the precipitation was performed strongly influenced the morphological properties (e.g. surface area and pore volume) and the composition of the oxygen carriers. Cyclic redox measurements over 10 cycles showed a high stability of all materials synthesized. The measurements also showed that the surface area of the materials had no significant effect on the CLC performance of the oxygen carriers. Importantly, CuO present in the form of CuAl₂O₄ was found to be fully reducible under CLC conditions.

In Chapter 3, the effect of the calcination temperature and CuO content on the redox performance of Al₂O₃- or MgAl₂O₄-stabilized oxygen carriers was studied. The results showed that the mechanical strength and structural properties of the oxygen carriers can be adjusted by a judicious choice of the calcination temperature. Moreover, a high calcination temperature shifted the reduction of CuO in N₂ towards higher temperatures. For Al₂O₃-stabilized CuO the reduction of CuAl₂O₄ in N₂ was not fully reversible, thus decreasing the oxygen release capacity of the Al₂O₃-stabilized oxygen carriers. On the other hand, no interaction between CuO and MgAl₂O₄ was observed, thus, yielding stable oxygen
carrying capacities close to the theoretical value for MgAl₂O₄-stabilized CuO. Performance tests in a fluidized bed revealed that only MgAl₂O₄-stabilized oxygen carriers containing ≤ 80 wt. % CuO were suitable for a continuous fluidized bed operation.

Inexpensive Al₂O₃-stabilized CuO with excellent CLC and CLOU performance can be obtained by inhibiting the formation of CuAl₂O₄. In Chapter 4, a Na⁺ doping strategy was developed to avoid the interaction between CuO and Al₂O₃. Furthermore, the effect of Na⁺ doping and redox cycling on the local structure and reduction pathways of CuO was studied using in-situ XANES spectroscopy. The acquired data revealed that the (apparent) rate of reduction increased with cycle number owing to an increase in structural disorder. Furthermore, the increasing rate of reduction changed the reduction pathway of CuO from a sequential (CuO → Cu₂O → Cu) to a direct (CuO → Cu) transition. Conductivity measurements demonstrated that Na⁺ doping enhanced the electronic transport kinetics possibly due to the generation of oxygen vacancies, leading in turn to an improved redox performance of Na⁺ doped oxygen carriers under CLC conditions. The absence of the CuAl₂O₄ phase in Na⁺-doped oxygen carriers also resulted in a high redox stability under CLOU conditions.

Carbon deposited on the oxygen carriers during the reduction reaction would yield the formation of COₓ during re-oxidation in the air reactor, thus, reducing the overall CO₂ capture efficiency of the chemical looping process. The CeO₂ₓ-stabilized, CuO-based oxygen carriers developed in Chapter 5 had an intrinsic ability to remove carbon precursors, thus, minimizing carbon deposition. Using Raman spectroscopy, it was confirmed that the oxidation of deposited carbon occurred via lattice oxygen of CeO₂ₓ. The materials synthesized possessed not only a high resistance to coke formation but also a high equilibrium partial pressure of O₂ and stable redox performance.

In Chapter 6, it was demonstrated that the formation of a CuO percolation network in CeO₂ₓ-stabilized CuO (percolation threshold between 20–30 wt. %) significantly affected the conduction characteristics of the material. Below the percolation threshold, conduction takes place via CeO₂ₓ bridges. Upon establishment of a CuO percolation network, solid state diffusion predominantly occurs via CuO/Cu bridges, which have a low energy barrier compared to CeO₂ₓ bridges. As a result, the activation energy for charge transport decreases with increasing CuO content, which in turn increases the rate of oxygen release and uptake.

Finally efforts were made to synthesize MgAl₂O₄-stabilized, Cu-modified, Fe₂O₃-based oxygen carriers for chemical looping water splitting. The development of this material was driven by the desire to obtain high and stable H₂ yield over many redox cycles.
while maintaining a low propensity for coke deposition when using inexpensive CH\textsubscript{4} as a fuel. Using temperature programmed experiments, it was revealed that the addition of Cu shifts the reduction of Fe\textsubscript{3}O\textsubscript{4} and FeO to slightly higher temperatures (using CH\textsubscript{4}), probably due to the fact that the activation of CH\textsubscript{4} on Cu is endothermic. EXAFS and EDX measurements showed that Cu and Fe did not mix. The partial coverage of surface Fe with Cu decreased the rate of CH\textsubscript{4} dissociation, which in turn reduced carbon deposition. During steam oxidation, MgAl\textsubscript{2}O\textsubscript{4}-stabilized Fe produced an equimolar mixture of H\textsubscript{2} and CO\textsubscript{x} owing to substantial carbon deposition via CH\textsubscript{4} decomposition. On the other hand, owing to their low tendency for coke deposition, Cu-modified materials produced hydrogen with very little CO\textsubscript{x} contamination. The experimental results obtained confirmed that Cu-modified, MgAl\textsubscript{2}O\textsubscript{4}-stabilized Fe\textsubscript{2}O\textsubscript{3} is a promising material for CH\textsubscript{4}-based water splitting.

\textbf{8.2 Outlook}

The large scale implementation of CLC and CLOU requires the “availability” of suitable oxygen carriers. There has been some encouraging progress in the synthesis and testing of new materials for CLC and CLOU. However, the thermodynamic, kinetic and charge transport characteristics of these new materials have to be determined in greater detail. Indeed, information of the charge transport parameters of supported metal oxides at practically relevant operating conditions are commonly not available in the literature. Therefore, it is important to develop the experimental tools to determine the ionic and electronic conductivity of oxygen carriers under oxidizing and reducing conditions.

Another aspect that deserves further research is a better understanding of the metal-support interactions. It seems that a high Tammann temperature of the support alone is not sufficient to ensure a high resistance to agglomeration. Indeed, some of the preliminary experiments indicate that mixing at the molecular or even atomic level is necessary to take full advantage of the stabilizing effect of high Tammann temperature supports. It has also been shown that a high calcination temperature increases the mechanical strength of the material, but at the cost of an increased crystallite size. However, the relationship between the structural properties (e.g. crystallite size) of the oxygen carrier and its activity is currently only poorly understood and requires further attention. A general issue concerning the assessment of the performance of oxygen carriers prepared by using different synthesis approaches is that there is no standardized protocol to characterize the CLC and CLOU
performance of the materials. Thus, it is currently impossible to link the physical properties of an oxygen carrier, which are critically influenced by the synthesis procedure, to its performance. Therefore, the CLC and CLOU community should establish standard protocols for performance testing and, indeed, also the morphological characterization of the materials, to allow the development of synthesis-structure-performance relationships.

Further, a better understanding of the influence of typical fuel impurities, such as alkali metals or sulfurous compounds, on the performance of the oxygen carrier is crucial to make chemical looping an attractive CCS technology for practical implementations. It is conceivable that alkali metal compounds of the coal ash can adversely affect the reactivity of the oxygen carriers and lead to agglomeration. Similarly, sulfur could lead to the irreversible formation of sulfides and sulfates. Therefore, it is essential to test oxygen carriers under practically relevant conditions, that is, taking into account the effect of typical fuel impurities on the performance of new materials. A very important aspect that has to be addressed in the near future is whether the development of synthetic materials that possess a high oxygen carrying capacity is an economically sound approach. This would require detailed techno-economic and life cycle assessment (LCA) taking fully into account the costs of material synthesis, kinetics and redox stability.
Appendix A: Experimental set-up

A.1 Fluidized bed reactor

A schematic diagram of the fluidized bed set-up used is shown in Figure A1. The reactor (i.d. 29.5 mm, length 460 mm) was constructed from quartz glass and contained a porous quartz frit as a gas distributor. The reactor was heated by an electric furnace (Carbolite MTF tube furnace) with the temperature of the fluidized bed being controlled via an N-type thermocouple. The flow rates of the inlet gases, viz. (i) 10 vol. % CH₄ in N₂, (ii) 10.5 vol. % O₂ in N₂, (iii) N₂ and (iv) air, were measured using calibrated rotameters and mass flow meters (AWM5101VN, Honeywell). The atmospheres in the reactor were switched via a computer-controlled set-up comprised of solenoid valves and a switch box. A fraction of the off-gas (1 L/min at 25 °C, 1 bar) was sampled via a quartz sampling tube and dehumidified via an anhydrous CaCl₂ trap. The composition of the water-free gas stream was determined by (i) a paramagnetic analyzer measuring O₂ (ABB Magnos27) and (ii) a non-dispersive infrared (NDIR) analyzer measuring CO, CO₂ and CH₄ (ABB Uras26).

Figure A1. Schematic diagram of the fluidized bed reactor set-up used.
A.2 Capillary reactor for X-ray absorption spectroscopy

A quartz capillary tube with an outer diameter and wall thickness of 1.0 mm and 0.1 mm, respectively, was used as the reactor. In order to optimize the transmission of X-rays and the pressure drop across the capillary cell, each oxygen carrier was mixed with boron nitride (ratio 1:2) and pelletized. The pellets were crushed and sieved in the size range 50–100 μm. The sample (~2 mg) was fixed in the capillary with two quartz wool plugs and heated under a flow of 5 vol. % O₂ in He to 750 °C using an air blower. The reduction and oxidation reactions were performed using 5 vol. % H₂ in He and 5 vol. % O₂ in He, respectively. Gas switching was performed using computer controlled valves. The total gas flow rate for all in-situ experiments was 25 mL/min. XAS measurements were taken in the center of the capillary reactor. A schematic diagram of the experimental set-up is shown in Figure A2. The capillary reactor was placed between the first and second ionization chamber that are filled with Ar and N₂, respectively. To account for the shift in the absolute energy of the incident X-rays due to the mechanical instability of the monochromator, a copper foil was placed between the second and third chambers to collect a reference spectrum. The off-gases were monitored using an on-line mass spectrometer (MS).

![Figure A2. Schematic diagram of the capillary reactor set-up used for in-situ XAS measurements (MS = mass spectrometer and MFCs = mass flow controllers).](image-url)
**A.3 Fixed bed reactor**

The reactor (i.d. 19.8 mm, length 590 mm) was made of recrystallized alumina and contained a perforated frit to support the bed. The reactor was heated by an electric furnace (Carbolite MTF tube furnace), the temperature of the bed being controlled via an N-type thermocouple. For all experiments, 0.5 g of an oxygen carrier (300–425 μm) was mixed with 5 g of Al₂O₃ (300–425 μm). This mixture was then sandwiched between layers of 1.4–1.7 mm Al₂O₃. The lower layer comprising Al₂O₃ and quartz wool prevented the material from falling through the holes in the perforated frit. The upper layer preheated the inlet gas which was supplied from the top of the reactor. The flow rates of the gases, viz. (i) 10 % CH₄ in N₂, (ii) N₂ and (iii) air were adjusted and recorded using calibrated mass flow meters (AWM5101VN, Honeywell). Liquid water was pumped at a rate of 12 mL/h via a syringe pump into an evaporator maintained at 210 °C. The resulting mixture comprising 15 vol. % steam in N₂ was fed via a heated line (also maintained at 210 °C) into the reactor. The atmosphere in the reactor was switched via a computer-controlled set-up comprising solenoid valves and a switch box. Steam present in the outlet gas was removed first by condensation via an ice bath and subsequently via a CaCl₂ trap. The composition of the effluent stream was analyzed continuously using (i) a non-dispersive infrared (NDIR) analyzer measuring CO, CO₂ and CH₄ (ABB Uras26), (ii) a paramagnetic analyzer measuring O₂ (ABB Magnos27) and (iii) a thermal conductivity analyzer measuring H₂ (ABB Caldos27). A schematic diagram of the fixed bed set-up used is shown in Figure A3.

![Figure A3. Schematic diagram of the fixed bed reactor set-up used.](image-url)
Appendix B: Experimental measurements

B.1 X-ray diffraction

In crystalline materials, lattice planes act as a diffraction grating for electromagnetic radiations with wavelengths of a similar order. For example, the ordered planes of a crystalline material scatter X-rays coherently in different directions. X-rays interfere constructively with a given lattice plane, when Bragg’s law

\[ 2d \sin \theta = n\lambda \]  

(B.1)

is satisfied, as shown in Figure B1. Here, \( d, \theta, n \) and \( \lambda \) are, respectively, the inter-planar spacing, the angle between the incident X-ray and the lattice plane, an integer number describing the order of diffraction and the wavelength of the incident X-ray. For X-ray diffraction analysis, the sample is typically grinded to a fine powder and subsequently placed in a beam of monochromatic X-rays. Since each crystallite in the powder is oriented randomly, in-house instruments equipped with a monochromatic X-ray source meet the Bragg condition by varying the angle of incidence. The resulting interference pattern of a crystalline material is its fingerprint and can be used to identify the material. If all phases in a material are identified, the methods of reference intensity ratio and Rietveld refinement can be used to determine the composition of the material. The reference intensity ratio method is based upon scaling all diffraction data to the diffraction of a standard reference material and can give quantitative results within ±10 wt. % of the actual composition. Unlike the method of reference intensity ratio, Rietveld refinement utilizes the entire diffraction pattern of a crystal structure and can estimate the composition with an accuracy of ±5 wt. %. Rietveld refinement provides also accurate information about the lattice parameters and atomic positions. Here, a crystal structure, along with information of the instrument (e.g. width of divergence slit) is used to generate a theoretical diffraction pattern. Subsequently, the theoretical line profile is refined using a least squares procedure until it matches the measured diffractogram. Finally, it is possible to obtain microstructural information from the line broadening and the shape of an X-ray diffractogram of a material. For a material comprising sub-micrometer size crystallites, the Scherrer equation (B.2) is commonly used to relate peak broadening with the average crystallite size, \( \text{viz.} \)
Here, $D$ is the crystallite size, $\beta$ is the full width at half maximum of the peak profile (corrected for instrumental broadening) and $K$ is the proportionality constant.

\[ D = \frac{K\lambda}{\beta \cos \theta} \quad (B.2) \]

**Figure B1.** Schematic illustration of Bragg’s law.

### B.2 Electron microscopy

**Figure B2.** Interaction between an electron beam and a solid sample.

A modern light microscope has a resolution of ~200 nm and a magnification in the range 1000–2000x. The resolution of a light microscope is limited by the wavelength of the light used for illumination. Since the wavelength of electrons is significantly shorter than the wavelength of visible light, electron microscopes allow the visualization of features that

152
would normally not be observable using optical microscopy. In electron microscopy, a sample is irradiated with a focused, monochromatic beam of electrons. The subsequent interactions between the sample and the electron beam (Figure B2) are detected and converted into an image. Electron microscopy can be divided into the following three categories: (i) scanning electron microscopy (SEM), (ii) transmission electron microscopy (TEM) and (iii) scanning transmission electron microscopes (STEM). In SEM, the surface of a sample is scanned line by line using a beam of electrons. The low energy secondary electrons knocked out from the surface of the sample (by the impinging electrons) are detected obtaining, thus, information about the sample’s topography. On the other hand, the impinging electrons that are back scattered by the nuclei of the sample are used to obtain an image contrast based on the atomic number of the atoms. The incoming beam of electrons may also cause the specimen atoms to emit characteristic X-rays. Energy dispersive X-ray (EDX) spectroscopy is used in SEM to perform elemental analysis of a selected area. By comparing the intensity of the EDX peaks of a sample and a standard, it is possible to determine semi-quantitatively the chemical composition of the sample. In TEM, a sample is exposed to a parallel beam of electrons. The electrons penetrating through a sample are focused by an objective lens and processed to obtain a magnified real image of the sample either on a fluorescent screen or on a monitor. The incoming electrons can be absorbed, scattered over small angles or diffracted, yielding in turn information about the thickness, composition and structure of the sample, respectively. For TEM, the sample has to be thin enough to allow the electrons to travel through it. Finally, STEM combines the principles of TEM and SEM.

**B.3 Fourier transform infrared spectroscopy**

Infrared (IR) spectroscopy is a non-invasive method probing molecular vibrations in gases, liquids, solutions, powders, films, surfaces, etc. IR spectroscopy utilizes the fact that most molecules, when subject to infrared radiation, perform vibrational or rotational motion. For a molecule to absorb infrared light, an electric dipole moment ($\mu$) must change due to rotation or vibration. Thus, diatomic gases without dipole moments (e.g. H$_2$ and O$_2$) are not detectable by IR spectroscopy. On the other hand, gases such as CH$_4$, CO$_2$ and CO can be identified by IR spectroscopy using mid-infrared radiations with wave numbers in the range 400–4000 cm$^{-1}$. In Fourier transform infrared (FTIR) spectroscopy, the incident infrared radiation is modulated in such a manner that the sample is exposed to all wavelengths
simultaneously. This arrangement results in an improved collection time, resolution and signal-to-noise ratio. IR spectroscopy can be performed either in transmittance or reflectance mode.

### B.4 Raman spectroscopy

Raman spectroscopy utilizes the vibrational motion of a molecule due to the inelastic scattering of incident photons. Due to the transfer of energy between the incident radiation and the scattering system, the incident photons either loss or gain energy. The Raman interaction in which the scattered photons have a lower energy compared to the incident photons is referred to as Stokes-Raman scattering. In anti-Stokes-Raman scattering, the scattered light has a higher energy compared to the incident light. The physical quantity that governs scattering is the polarizability ($\alpha$). To be Raman active, a molecule must have anisotropic polarizability, *i.e.* the polarizability of a molecule must change during the vibration. Molecules containing aromatic rings, conjugated functional groups, double bonds or free electron pairs show strong Raman signals because the delocalized electrons in these molecules are easily polarizable. Raman spectroscopy is particularly useful for the identification of inorganic compounds that have low vibrational frequencies lying close to or even below 400 cm$^{-1}$, which is generally the limit for IR spectroscopy.

### B.5 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) allows us to probe the electronic and structural properties of a material. When X-rays pass through a material of thickness $x$, their intensity decreases according to Lambert’s Law:

$$I_t = I_0 e^{-\mu(E)x} \quad (B.3)$$

where $I_0$ and $I_t$ are the intensities of the incident and transmitted X-rays, respectively, and $\mu(E)$ is the linear absorption coefficient, which is a function of the photon energy ($E$). A sharp rise in absorption (referred to as absorption edge, $E_{edge}$) is observed when X-rays have sufficient energy to excite a core level electron of an atom to a vacant excited state or the continuum. The fact that a specific X-ray photon energy is required to excite core electrons makes XAS an atomic probe. The excited photoelectron can be considered as a spherical wave with wavenumber $k$:
where, $\lambda$ is the wavelength, $m$ is the electron mass, $h$ is the Planck’s constant and $E_0$ is the binding energy of the photoelectron. The outgoing wave scatters off neighboring atoms, producing a back scattered wave. The interference between the outgoing and back scattered waves results in a modulation of the absorption coefficient. As a consequence, the absorption coefficient above $E_{\text{edge}}$ is given as

$$
\mu_{\text{total}} = \mu_0 \left[ 1 + \chi(k) \right]
$$

(B.5)

where $\mu_0$ is the absorption coefficient that would be observed in the absence of interference effects and $\chi(k)$ is the oscillatory part of the observed absorption coefficient and contains information about the local structure around the absorbing atom. An X-ray absorption spectrum is typically divided into two regions, viz. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). XANES spectroscopy provides information about the oxidation state, site symmetry and vacant orbitals of the absorbing atom. On the other hand, EXAFS spectroscopy is sensitive to the local environment around the absorbing atom and is therefore used to determine the coordination number, inter-atomic distance, Debye-Waller factor (which accounts for the disorder in a material due to the thermal vibrations and static displacements) and type of atoms surrounding the absorbing atom.

### B.6 Gas adsorption analysis

Gas adsorption analysis allows the determination of the specific surface area, pore volume and pore size distribution of a porous material. The physical adsorption of a gas on a solid surface occurs due to weak van der Waals forces between the gas molecule (adsorbate) and the solid surface (adsorbent). Gas adsorption is characterized by an adsorption isotherm, which relates the quantity of gas adsorbed on a surface to the relative pressure $P/P_{\text{sat}}$, where $P_{\text{sat}}$ is the saturation pressure of the gas at a fixed temperature. The Brunauer-Emmett-Teller (BET) equation is the most widely used model to calculate the surface area from the measured adsorption isotherm. The BET theory assumes that at the saturation pressure, the number of layers of gas molecules adsorbed on the surface is infinite. The adsorption of the first layer of gas molecules is governed by the heat of adsorption, while adsorption of
subsequent layers is governed by the heat of condensation. The BET equation relates the quantity of gas adsorbed (W) with the relative pressure as

\[
\frac{1}{W} \left( \frac{P_{\text{sat}}}{P} - 1 \right) = \frac{1}{W_m C} + \frac{C-1}{W_c C} \left( \frac{P}{P_{\text{sat}}} \right)
\]

where \(W_m\) is the quantity of adsorbate required to form a monolayer on the surface and C is a constant > 1. The BET equation requires a linear relationship between \(1/[W(P_{\text{sat}}/P)-1]\) and \(P/P_{\text{sat}}\), which is typically only the case for \(P/P_{\text{sat}} < 0.3\) (i.e. before small pores have been filled completely with the adsorbate). The total surface area of the sample is then given by

\[
S = \frac{W_m A_{cs} N}{M}
\]

Here, \(N\) is the Avogadro’s number. \(M\) and \(A_{cs}\) are, respectively, the molecular weight and cross-sectional area of the adsorbate.

The materials’ pore structure can be determined by allowing the adsorbate to condense in the pores. At \(P/P_{\text{sat}} = 1\), capillary condensation and physical adsorption ensures that all pores are filled with liquid. As the relative pressure is decreased, the adsorbate starts to evaporate first from the pores with the largest diameter. The Barrett-Joyner-Halenda (BJH) model relates the quantity of the adsorbate evaporated to the pore size. The BJH model is based on the Kelvin equation (which relates the pore radius to the condensation pressure) and assumes cylindrical pores with a radius equal to the sum of the Kelvin radius (the radius of the condensed adsorbate) and the thickness of the adsorbed gas layer on the pore wall. For \(N_2\), the Kelvin radius (\(r_k\) in Å) is related to the relative pressure \(P/P_{\text{sat}}\) by

\[
r_k = \frac{4.15}{\log \left( \frac{P_{\text{sat}}}{P} \right)}
\]

Since measurements near the limits of \(P/P_{\text{sat}}\) (i.e. at 0 and 1) are impracticable, typically the limit \(0.01 < P/P_{\text{sat}} < 0.95\) is used for the BJH model. This corresponds to mean pore diameters of 2–200 nm (using \(N_2\)).
B.7 Conductivity measurements

![Figure B3](image)

**Figure B3.** 4-point configuration to measure the electrical conductivity of a CuO-based pellet sintered at 1000 ºC for 24 h.

Conductivity measurements were used to characterize the electrical properties of a material. The conductivity (or resistivity) of a material can be measured using either a 2-point or 4-point technique. In 2-point probes, a current ($I$) is passed through a material of well-defined geometry using two metallic wires. The same wires are used to measure the voltage ($V$) across the material. The resistance ($R$) of the material is given by:

$$ R = \frac{V}{I} \quad \text{(B.9)} $$

The conductivity ($\sigma$) of the material can be calculated from the following relation:

$$ \sigma = \frac{1}{\rho} = \frac{l}{R(wh)} \quad \text{(B.10)} $$

where $w$, $h$ and $l$ are the physical dimensions of the material and $\rho$ is the resistivity. Since the contact wires also have some resistance, measuring conductivity with a 2-point technique is often not reliable. This problem can be overcome by using a 4-point measurement technique. In a 4-point probe, four wires are attached to the sample as shown in Figure B3. Passing a current through two wires and measuring the voltage through the other two wires allows the measurement of the sample’s resistance only. The accuracy of the 4-point measurements should be validated by measuring the voltage through the wires previously used for the current and vice versa. The difference between the two measured resistances
should not exceed 10 %. For conductivity measurements, the sample should be homogenous, isotropic and without any holes. Furthermore, the sample should also have a uniform thickness and flat surfaces.

B.8 Thermogravimetric analysis

Thermogravimetric analysis is a technique in which the weight change of a sample is monitored continuously as a function of temperature or as a function of time at a fixed temperature in a controlled environment. Since the weight of a sample changes during redox reactions, thermogravimetric analysis is very useful in studying the redox characteristics and kinetics of materials. However, in thermogravimetric analysis experimental parameters, such as initial sample weight, crucible size, temperature ramp rate etc. can affect significantly the recorded weight change profiles. Therefore, to compare the weight change profiles from different experiments, it is necessary to standardize the operating parameters.
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PUBLICATIONS


A. Tsoukalou, Q. Imtiaz, S. M. Kim, P. M. Abdala, S. Yoon and C. R. Müller, Development of MgAl$_2$O$_4$-stabilized, Dry-reforming of methane over bimetallic Ni-M/La$_2$O$_3$ (M = Ni, Co, Fe): The effect of the rate of La$_2$O$_2$CO$_3$ formation and phase stability on the catalytic activity and stability, J. Catal., In press, 2016.


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**EXPERTISES**

TEM, Raman spectroscopy, FTIR, XANES spectroscopy, EXAFS spectroscopy, XRD, GC, MS, electrical conductivity measurements, N$_2$ physisorption analysis, chemisorption, thermogravimetric analysis, fluidized and fixed bed reactors.