Investigation on the decrease in the reduction rate of oxygen carriers for chemical looping combustion

Citation for published version (APA):

San Pio Bordeje, M. A., Roghair, I., Gallucci, F., & van Sint Annaland, M. (2016). Investigation on the decrease in the reduction rate of oxygen carriers for chemical looping combustion. *Powder Technology*, 301, 429–439. <https://doi.org/10.1016/j.powtec.2016.06.031>

Document license:
TAVERNE

DOI:
[10.1016/j.powtec.2016.06.031](https://doi.org/10.1016/j.powtec.2016.06.031)

Document status and date:
Published: 01/11/2016

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Investigation on the decrease in the reduction rate of oxygen carriers for chemical looping combustion

M.A. San Pio, I. Roghair, F. Gallucci, M. van Sint Annaland *

Chemical Process Intensification, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 11 March 2016

Received in revised form 18 May 2016

Accepted 15 June 2016

Available online 16 June 2016

Keywords:

CO₂ capture

Chemical looping combustion

Cu-based oxygen carriers

Oxygen uncoupling

Diffusion limitations

ABSTRACT

Copper oxide on alumina is often used as oxygen carrier for chemical looping combustion owing to its very high reduction rates at lower temperatures and its very good mechanical and chemical stability at not too high temperatures. In this work, the redox kinetics of CuO/Al₂O₃ have been measured and analysed with many consecutive reduction (50% H₂, 50% N₂) and oxidation (air) cycles at different temperatures using thermogravimetric analysis. In all the redox cycles, a cyclic steady state in the redox kinetics is observed after several redox cycles, where a sudden decrease in the reaction rate is observed after a certain solids conversion, typically around 75%, depending in particular on the operating temperature. Models developed in the literature fail at predicting these redox kinetics and they are mostly shrinking core/grain type models with an ad-hoc combination and modification of chemical reaction and gas phase diffusion. The oxygen carrier was characterized in detail with different techniques including N₂ physisorption, XRD and SEM-EDX to investigate morphological changes in the particle over the redox cycles in order to better understand why all the models developed in literature fail. After the study we can conclude that i) gas-phase diffusion is not playing a limiting role on the redox kinetics despite significant morphological changes in the particle; ii) migration of copper from the inside of the particle to the surface of the particle does not occur or does not influence the kinetics; iii) oxygen uncoupling is not influencing the kinetics being equally fast for Cu₂O and CuO, although it can be significant for the final maximum particle conversion; iv) solid phase oxygen diffusion limitations may be responsible for the observed drop in reaction rate.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Concerns about the role of anthropogenic greenhouse gas emissions, mainly CO₂ emissions generated by the combustion of fossil fuels [1,2,3,4], on the observed climate change have resulted in great research efforts to develop new technologies that can reduce the emission of (in particular) carbon dioxide into the atmosphere. Carbon Capture and Storage (CCS) provides a reasonable mid-term solution to mitigate CO₂ emissions, until sustainable resources will be able to substantially replace fossil fuels.

Several possible technologies are being investigated to enable CCS from power plants [5,6,7,8,9,10,11]. In particular chemical-looping combustion (CLC) has proven to be a very promising combustion technology for new power production plants with integrated CO₂ capture, as well as for hydrogen production from natural gas [12,13], yielding the lowest energy penalties for the capture stage. The principle features a metal oxygen carrier (Me/MeO) that is alternately reduced by a fuel (syngas or

natural gas) in a fuel reactor and oxidized by air in an air reactor operating at atmospheric pressure.

In the fuel reactor the following reactions take place, if syngas is used as fuel:

The reduced oxygen carrier is regenerated in the air reactor by reaction with the oxygen from the incoming air (Eq. (3)):

Since the separation of oxygen from nitrogen is already performed in the air reactor, a nitrogen free CO₂ stream is obtained from the fuel reactor.

CLC is especially competitive when it is operated at high temperatures (1000–1200 °C) and high pressures (15 bar or higher) [14], but these conditions may pose major technical problems to concepts based on interconnected fluidized-bed reactors. Dynamically operated

* Corresponding author.

E-mail address: M.v.SintAnnaland@tue.nl (M. van Sint Annaland).

Fig. 1. Comparison of TGA experiments and ad-hoc shrinking core models (SCM, CGSM) for $\text{CuO}/\text{Al}_2\text{O}_3$.

packed bed reactors [15], where the oxygen carrier is stationary and is alternately reduced and oxidized via periodic switching of the fuel and air streams, may circumvent such problems, and have been shown to provide a good alternative to fluidized bed technology, especially for pressurized systems [16]. Hamers et al. [17] found that a large temperature rise can be avoided by carrying out CLC in two packed-bed

reactors placed in series in a two-stage CLC (TSCLC) process, lowering the requirements for the selected oxygen carriers and reactor materials, while hardly sacrificing in energy efficiency. In particular, the TSCLC concept allows the use of copper oxide on alumina in the first stage, taking advantage of its very high reduction rates at lower temperatures and its very good mechanical and chemical stability [16,18], while mitigating problems with agglomeration formation commonly seen with Cu-based oxygen carriers at higher temperatures, because of the low melting point of Cu, 1085 °C.

Accurate knowledge of the redox kinetics of the oxygen carriers is extremely important for the modelling of chemical looping processes, and in particular for packed-bed CLC processes, as they determine to a large extent the amount of fuel slip, and consequently the overall process efficiency. In particular a better understanding and description of the sudden strong decrease in reaction rate at a certain particle conversion, typically at around 75% at 800 °C and 65% at 600 °C, is required. Until now, researches have attempted to describe the redox kinetics with a shrinking core or grain type model (SCM) or a changing grain size model (CGSM) using a combination of chemical reaction control and gas-phase diffusion control regimes, assuming that gas-phase diffusion limitations were responsible for the decrease in reaction rate [19, 20]. Several ad-hoc models have been developed and published in the open literature that try to predict the redox kinetics of several oxygen carriers at different temperatures, but they fail to describe the above mentioned sudden drop in reaction rate [21,19,22,20], especially when it comes to its dependence on the temperature.

Fig. 1 illustrates a comparison of these different ad-hoc models, variations of shrinking core models, with experimental data carried out in

Fig. 2. TGA setup used in this work.

the thermogravimetric analyser (TGA) for CuO/Al₂O₃ at different temperatures. While the initial kinetics can be predicted accurately, they clearly fail to describe the decrease in reaction rate, temperature dependency and final conversion. Note that, contrary to fluidized-bed CLC concepts which operate with a relatively small difference in the degree of oxidation state of the oxygen carrier between the air and fuel reactor, in packed-bed CLC the particle conversion is always (in the major part of the bed) cycling between the two extrema, making it very important to understand and predict the maximum achievable particle conversion. Similar redox kinetics behaviour has been observed for different oxygen carriers, such as ilmenite (Fe₂O₃/Ti₂O₅) and NiO/Al₂O₃.

The reduction mechanism of CuO is very complicated, occurring in one step from CuO to Cu only under an excess supply of hydrogen. Otherwise it occurs under a sequential pathway [23] for a change in oxidation of state from “+2” to 0 (CuO → Cu₄O₃ → Cu₂O → Cu).

For Cu/CuO on alumina particles also the spinel forms (CuAlO₂, CuAl₂O₄) could play a role according to the following reactions:

Four different causes could cause this sudden decrease in reaction rate: a) morphological changes in the particle, b) changes in the solid phases or distribution of the solid phases, c) oxygen uncoupling reaction [24], d) solid phase oxygen diffusion.

Oxygen uncoupling is a thermal decomposition of the CuO where the following reaction occurs [24]:

This reaction occurs under N₂ environment or under a limitation of the H₂ in the reduction of CuO.

This study aims at a better understanding of these phenomena in Cu/Al₂O₃-based oxygen carriers [25], and their role in determining the change in reaction rate at high solids conversions [26], which is the first step in the further development of a reliable model to predict the particle conversion.

The objectives of this paper are (i) to investigate the morphological changes that occur in the particle over many consecutive redox cycles, and ii) to elucidate the real cause of the sudden decrease in the reaction rate at higher particle conversions for a CuO/Al₂O₃ oxygen carrier. After a description of the experimental techniques, the results of TGA experiments of the oxygen carrier over many consecutive redox cycles are presented and discussed. Moreover, BET, XRD and SEM-EDX results are analysed in detail to characterize the oxygen carrier, investigate the morphological changes in the particle and elucidate which of the above-mentioned possible causes can be responsible for the sudden decrease in the observed reduction rate.

2. Material and methods

2.1. Redox reactivity

The experiments have been carried out with a 12.5 wt% CuO/Al₂O₃ oxygen carrier (1.1 mm diameter - Sigma-Aldrich). TGA is used to measure and analyse the oxygen carrier reactivity. The TGA consists of a cylindrical quartz reactor (15 mm i.d.) placed in an oven that can be operated at up to 1200 °C and atmospheric pressure. A schematic

Fig. 3. Comparison of the reduction conversion with particles or powder for CuO/Al₂O₃ at 800 °C.

Fig. 4. Oxygen carrier conversion for reduction with 50% H₂ and 50% N₂ for CuO/Al₂O₃ at, a) 800 °C, b) 600 °C.

Fig. 5. SEM images of a) fresh CuO/Al₂O₃, b) 50 redox cycles CuO/Al₂O₃, c) 100 redox cycles CuO/Al₂O₃ at 800 °C.

representation of the setup used is shown in Fig. 2. A sample (typically about 100 mg) is placed in a quartz sample-holder (40 μm pore size) connected to a CI Precision microbalance with a platinum wire. The temperature and weight of the sample are continuously monitored. Gas flow rates are controlled by Mass Flow Controllers (Bronkhorst) with the total gas flow rate set at 480 mL/min. It has been proven, by using different flow rates, that the measured reactivity is not influenced by external mass transfer limitations [27]. The gas is fed from the bottom part of the reactor. The lines at the outlet of the TGA are traced in order to avoid steam condensation.

The reactivity experiments have been carried out using consecutive redox cycles using 50% H₂ and 50% N₂ for the reduction cycles and air during the oxidation cycles, at different temperatures ranging from 600 °C to 800 °C. Redox cycles consist of 15 min reduction and 10 min

oxidation with two minutes purge (with nitrogen) between the reduction and oxidation cycles to avoid mixing of the different reactants.

The oxygen carrier conversion (X_s) is subsequently calculated from the observed mass change in the oxygen carrier under different experimental conditions, defined by Eq. (10), where m is the current mass and m_{ox} and m_{red} are the mass of the fully oxidized and reduced forms of the oxygen carrier. The fully oxidized mass is taken as the mass of the fresh material which was delivered in oxidized form. Eq. (10) is the equation used to calculate the reduction conversion of all the experiments presented in this work, being m the initial mass, and m_{red} and m_{ox} the mass in the reduced and oxidized state respectively.

$$X_s = \frac{m - m_{red}}{m_{ox} - m_{red}} \quad (10)$$

Table 1
BET and density results for different number of redox cycles of CuO/Al₂O₃ at 800 °C.

Experiment	Surface area (m ² /g)	Mean pore diameter (nm)	Pore volume (cm ³ /g)	Pore size range (nm)	Skeletal density (g/cc)
Fresh CuO/Al ₂ O ₃	227.07	8.51	0.45	[1–14]	3.20
10 redox cycles CuO/Al ₂ O ₃	63.08	15.59	0.39	[1–60]	3.80
25 redox cycles CuO/Al ₂ O ₃	33.66	28.68	0.33	[1–80]	4.81
50 redox cycles CuO/Al ₂ O ₃	33.15	35.50	0.32	[1–100]	3.31

a)	Fresh CuO/Al ₂ O ₃	8 redox cycles CuO/Al ₂ O ₃
a) Particle surface
b) Inside the particle

b)

Fig. 6. a) Contrast-enhanced EDX images of Cu for fresh CuO/Al₂O₃, 8 redox cycles CuO/Al₂O₃ at 800 °C of a) surface of the spherical particle, b) inside the particle cutting it with Epoxi resin.
b) SEM images of the surface and inside of the particle.

Table 2

Quantitative ratio analysis of CuO/Al₂O₃ at different number of redox cycles in the surface of the particle or inside the particle.

Mass ratio	Surface particle		Cut particle	
	Cu/O	Cu/Al	Cu/O	Cu/Al
Fresh CuO	0.383	0.383	0.237	0.176
8 redox cycles	0.690	0.616	0.266	0.138
50 redox cycles	0.567	0.471	–	–
100 redox cycles	0.598	0.490	–	–

2.2. Oxygen carrier characterization

The surface area and pore size distribution of all the oxygen carrier samples before and after the experiments was determined by the Brunauer-Emmett-Teller (BET) method by adsorption/desorption of nitrogen at 77 K in a Thermo-Scientific Surfer. A gas expansion pycnometer (Quantachrome Ultrapyc 1200e) has been used to measure the volume of a weighted sample of the solid carrier, from which the skeletal density can be calculated. This value is also used in the BET-method to determine the specific surface area. In addition, the microstructure of different samples was analysed in a FEI Quanta 3D FEG scanning electron microscope combined with Energy-Dispersive X-ray spectroscopy (SEM-EDX) to measure the difference in pore size and the distribution of the chemical elements in the oxygen carrier. Crystalline species were identified by X-Ray Diffraction (XRD) in a Rigaku diffractometer at 298 K with a mobile Cu anode.

3. Results and discussion

3.1. Redox cycles

The total flow rate during the reduction and oxidation cycles as well as the purge were set at 480 mL/min. With this flow rate mass transfer limitations can be avoided while keeping the disturbance of the balance to a minimum [27]. Before starting the experiments, it was verified that indeed external mass transfer limitations do not occur in these TGA experiments. Two TGA experiments were carried out. Firstly, 40 redox cycles were carried out in the TGA under standard conditions. Subsequently, these used particles were crushed to fines and introduced again in the TGA to perform 5 more redox cycles. The particle conversion during the reduction cycle before and after crushing the particles is shown in Fig. 3. Particle Size Distribution, PSD, was done for the crushed particles obtaining a distribution of [80–355 µm], with a mean size of 195 µm.

Fig. 3 shows how both, the slope of the reaction rate and the final conversion are virtually the same, confirming that the particle size does not affect the redox kinetics and thus that external mass transfer limitations in the TGA experiments are insignificant.

3.1.1. Reactivity

The reduction kinetics strongly depends on the operating temperature. The redox kinetics were monitored over many consecutive redox

Fig. 7. Cu wire redox reaction a) Reduction conversion, b) Oxidation conversion.

cycles for two different temperatures, viz. 600 °C and 800 °C. The oxygen carrier conversion during the reduction cycle with 50% H₂ and 50% N₂ at 800 °C is plotted after a different number of redox cycles in Fig. 4a. The oxygen carrier was tested over >200 redox cycles to check its reproducibility. It was observed that the oxygen carrier reaches its steady state maximum conversion after the second cycle, while the initial slope (initial kinetics) remains essentially unchanged. It can be observed that the reduction kinetics is very fast over the first 20 s of the reduction cycle, and afterward there is a sudden drop in the reaction rate when the particle conversion approaches approximately 70%.

The oxygen carrier conversion during the reduction reaction with 50% H₂ and 50% N₂ at 600 °C is shown in Fig. 4b. The same trend in

Table 3

XRD Phases with the number of redox cycles at 800 °C.

Phase name	Formula	Fresh CuO/Al ₂ O ₃	25 redox cycles finished in oxidation	75 redox cycles finished in oxidation	100 redox cycles finished in oxidation	100 redox cycles finished in reduction
Tenorite	CuO	✓	✓	✓	✓	✓
Aluminium oxide	Al ₂ O ₃	✓	✓	✓	✓	✓
Gamma-alumina	Al ₂ O ₃	✓	✓	✓	✓	✓
Copper dialuminium oxide	CuAl ₂ O ₄	✓	✓	✓	✓	✓
Cuprite	Cu ₂ O			✓	✓	✓
Copper (I) aluminium oxide	CuAlO ₂			✓	✓	
Copper	Cu					✓

Table 4
Experiments to evaluate the existence of oxygen uncoupling.

Number of experiment	Description
1	5 CLOU cycles finished in oxidation state at 800 °C
2	8 CLOU cycles finished in uncoupling state at 800 °C
3	35 CLOU cycles finished in uncoupling state at 800 °C
4	3 CLOU cycles finished in oxidation state + 1 h reduction state at 800 °C
5	3 CLOU cycles finished in uncoupling state + 1 h reduction at 800 °C
6	3 CLOU cycles finished in uncoupling state + 1 h reduction state at 600 °C
7	Fresh CuO/Al ₂ O ₃ + 1 h oxidation + 2 days of N ₂ at 870 °C + 1 h reduction at 800 °C
8	Fresh CuO/Al ₂ O ₃ + 1 h oxidation + 2 days of N ₂ at 870 °C + 1 h reduction at 600 °C
9	8 redox cycles finished in oxidation state + 1 h N ₂ at 800 °C
10	35 redox cycles finished in oxidation state + 1 h N ₂ at 800 °C
11	50 redox cycles finished in oxidation state + 1 h N ₂ at 800 °C

kinetics is observed: fast kinetics in the first 20 s of the reduction cycle with a sudden drop in the reaction rate, but in this temperature at a slightly lower percentage of particle conversion of around 60%. Very similar behaviour was observed for the oxygen carrier conversion during the oxidation cycles with air at both temperatures, as well as for several other oxygen carriers such as NiO/Al₂O₃ and ilmenite (Fe₂O₃/Ti₂O₅) (not shown here for brevity).

3.2. Oxygen carrier characterization

In order to explain why the oxygen carrier reaction rate drops after a certain particle conversion, the particle morphology and chemical composition were followed using BET, SEM-EDX and XRD for samples having experienced a different number of redox cycles.

SEM images of the fresh CuO/Al₂O₃ oxygen carrier and after 50 and 100 complete redox cycles in the TGA are shown in Fig. 5.

An increase in void fractions as well as the formation of cracks is clearly visible for particles having experienced a larger number of redox cycles. Although the void fraction increases significantly with the number of cycles, this does not influence the redox kinetics, which are virtually constant after the second cycle (see Fig. 5a and b).

The surface area, mean pore size diameter, pore volume and pore size range for several experiments after a different number of redox

Fig. 8. Oxygen uncoupling conversion after different treatment of the oxygen carrier (the experiments are explained in Table 4).

Table 5
Experiments to evaluate the influence of the oxygen uncoupling on the redox kinetics.

Number of the experiments	Description
1	1 h N ₂ at 870 °C + 1 h reduction at 800 °C
2	1 h N ₂ at 870 °C + 1 h reduction at 600 °C
3	2 days N ₂ at 870 °C + 1 h reduction at 800 °C
4	2 days N ₂ at 870 °C + 1 h reduction at 600 °C

cycles at 800 °C measured with BET analysis are summarized in Table 1. The surface area strongly decreases with the number of redox cycles.

Remarkably, this change in surface area is not affecting the kinetics, because the kinetics already reach a cyclic steady state after two complete redox cycles, while the surface area continues to decrease. The decrease in surface area is probably related to sintering of the alumina (and Cu), however, the Cu remains accessible since the kinetics and final conversion are constant over many cycles.

The mean pore diameter increases significantly with the number of redox cycles and also the pore size distribution widens, which is in agreement with the changes observed in the SEM images, where there is an increase in void fraction. From the mean pore diameter results, it

Fig. 9. a) Reduction reactions at 800 °C, b) Reduction reactions at 600 °C after different oxygen uncoupling conditions (1 h N₂ at 870 °C or 2 days N₂ at 870 °C) for CuO/Al₂O₃ (experiments from Table 4).

is clearly visible how the micro-pores shift towards macro-pores as a function of the number of redox cycles. The pore volume decreases with the number of redox cycles, whereas no significant change in bulk density was observed as a function of the number of redox cycles.

These results imply that the change in particle morphology cannot be responsible for the observed drop in reaction rate in the redox reaction kinetics at high particle conversions.

The distribution of copper in the particles is measured using EDX-mapping on fresh and redox cycled-samples, studying both the outer surface of the particles as well as the particle interior. For the latter, the particles were cut with a diamond sheet after being embedded in an epoxy resin. All the EDX images were contrast-enhanced in GIMP 2.

EDX images of copper for the particle external surface and the inside of a cut particle of a fresh CuO/Al₂O₃ particle and after being exposed to 8 redox cycles at 800 °C can be found in Fig. 6, and a quantitative analysis of the element ratios of copper, oxygen and alumina, Cu/O and Cu/Al, are shown in Table 2 after the reduction reaction.

Fig. 6a shows a significantly higher concentration of copper in the bulk after several consecutive redox cycles, confirmed by the results in Table 2 showing higher Cu/O ratios for samples having experienced several redox cycles. It can also be observed that the fresh particles already have an inhomogeneous distribution of copper as the core of the particles already has lower Cu/O and Cu/Al ratios compared to the outer surface. The inhomogeneous distribution of copper on the fresh particle can be attributed to the preparation method of the CuO/Al₂O₃ particles, where a temperature treatment is confirmed by Sigma-Aldrich. These measurement results are inconclusive whether agglomeration of copper takes place on the external surface of the particle or whether there is a migration of copper from the inside of the particle to the external surface over the many redox cycles (because a mapping with EDX shows

only an estimation of how the copper is distributed in the bulk), but it is clear that it does not affect the redox kinetics, since a cyclic steady state in the kinetics was obtained already after the second cycle (see Fig. 4). This supports the fact that gas-phase diffusion limitations cannot explain the sudden decrease in the observed reaction rate.

XRD measurements were carried out to investigate possible changes in the phases in the samples having experienced more redox cycles. The results are summarized in Table 3, where the formation of Cu₂O is observed after 75 redox cycles, and the amount of CuAl₂O₄, according to the intensity of the XRD patterns, is higher. The higher intensity is merely an indication and not a quantitative analysis, due to it shows not only the intensity but also the size of the crystal. A larger amount of CuAl₂O₄ can shift the following equilibrium (Eq. (5)) and increase the amount of Cu₂O, high enough to be detected in the XRD analysis. The Al₂O₃ is turned into gamma-alumina, as could be expected according to literature at high temperatures (800 °C) [28].

In literature [23] the reduction of CuO involves an induction period embedding H into the bulk of CuO that could cause the drop in reaction rate. However, the drop in reaction rate is also observed when reacting the CuO with CO, indicating that the induction time for embedding of H cannot be the only explanation for the observed phenomena. Additionally, even in the fresh material both, CuAlO₂ and CuAl₂O₄, are detected, possibly indicating that the accessible Cu is lower than may be expected according to the oxygen carrier specifications. Moreover, these phases are reduced slower than CuO and Cu₂O. This can be explained because spinel is more resistant due to stabilizing effect of the spinel structure, having slower kinetics than the reduction of CuO and Cu₂O to Cu.

Fig. 10. SEM images of a) 5 CLOU cycles, b) 8 CLOU cycles, c) 35 CLOU cycles at 800 °C for CuO/Al₂O₃.

Therefore, we think that the drop in reaction rate is more related to the rate of spinel reduction and to oxygen vacancies diffusion rather than the embedding of the hydrogen.

The presence of Cu_2O was observed indistinctly in the oxidized and reduced state even at 800 °C, where it is well-known that the formation of Cu_2O takes place at higher temperatures, above 870 °C [26,29,30]. Especially the presence of Cu_2O in the reduced oxygen carrier is an indication that this component has a much lower reaction rate than CuO and it could be responsible for the observed drop in reaction rate. CuO and Cu_2O may somehow be shielded during the reduction cycle, because these phases should not be present after the reduction with H_2 , where maximum particle conversion seems to have been achieved. This assumption is corroborated by TGA experiments carried out with a Cu wire (assuming 99 wt% Cu). In the experiments is observed how the reduction from CuO to Cu occurs immediately in about 2 min, while the oxidation is not complete even after 4 h (see Fig. 7). This supports the idea that CuO can be shielded making it difficult to reach it, which may be an indication of solid diffusion limitations. To elucidate this further, experiments have been carried out such that Cu_2O is produced in the oxygen carrier via oxygen uncoupling, as described in the following sections [31].

3.3. Oxygen uncoupling

After verifying again the absence of external mass transfer limitations, the experiments summarized in Table 4 were carried out to study in more detail the possible influence of chemical looping oxygen uncoupling (CLOU) on the kinetics. A CLOU cycle refers to 1 h oxidation

with air followed by 1 h of N_2 (uncoupling) at 800 °C. The reduction cycle was always carried out with 50% H_2 and 50% N_2 for 15 min with a total flow rate of 480 mL/min.

The N_2 used in these experiments has a 99.999% purity (with $\text{O}_2 < 4$ ppm) according to the specifications (Linde gas).

Fig. 8 reports the oxygen uncoupling conversion after different pre-treatment conditions of the oxygen carrier. The experiments shown are experiments 1–3, 9 and 11 to simplify the graph. It can be clearly observed that the oxygen uncoupling reaction is much slower than the previously shown gas/solid reduction reactions, and can account for a conversion of about 10% of the carrier material. The reaction rate decreases after a few minutes and the conversion only slightly increases afterwards.

It is interesting to see that the difference in the maximum conversion achieved at 800 °C and 600 °C is around 10% (from Fig. 4), being 75% of conversion at 800 °C and 65% conversion at 600 °C, respectively. The difference in particle conversion corresponds to the oxygen uncoupling conversion obtained in the experiments shown in Fig. 8. As oxygen uncoupling hardly occurs at 600 °C, comparing the two figures it seems that at 600 °C we are able to convert all the accessible CuO via gas/solid reactions, while at 800 °C additional conversion is achieved via oxygen uncoupling.

It is also observed that the oxygen uncoupling reaction rate is not affected whether previously redox cycles or CLOU cycles have been performed. The treatment done to the particle before the oxygen uncoupling does not affect the CLOU kinetics.

To assure a steady-state in oxygen uncoupling conversion, the same oxygen uncoupling reaction was carried out for a much longer time

Fig. 11. SEM images of a) 8 CLOU cycles, b) 8 redox cycles, c) 35 CLOU cycles, d) 35 redox cycles at 800 °C for $\text{CuO}/\text{Al}_2\text{O}_3$.

period of 15 h at 870 °C, because it is known from previous studies reported in the literature that at this temperature the maximum conversion can be achieved [26,29,30]. Four different experiments were carried out in order to compare the influence of the oxygen uncoupling on the redox kinetics as summarized in Table 5.

In Fig. 9, the experiments of 1 h reduction at 800 °C and 1 h of reduction at 600 °C after different oxygen uncoupling cycles at 870 °C are reported. To make a better comparison of the reduction kinetics, the two graphs are plotted after 1 h (note that 15 h of oxygen uncoupling lead to about 20% conversion, and this is the starting value for the reduction).

It can be seen that the reaction rate of the reduction reaction at 800 °C is the same independent of the oxygen uncoupling conversion reached before. Both have the same slope in kinetics, although the final conversion is a slightly higher (around 3%) for the case where the reaction was carried out after 15 h of N₂ feeding, where the initial amount of Cu₂O is higher before the reduction was started. This indicates that the additional Cu₂O resulting from the uncoupling is reduced faster. Also a reduction cycle at 800 °C after being previously oxidized is plotted in the same graph, showing that the kinetics are basically the same as when reducing after oxygen uncoupling.

The reaction rate of the reduction reaction at 600 °C follows the same trend as for 800 °C, showing similar kinetics after 1 h or 15 h of oxygen uncoupling and that the conversion after 15 h of oxygen uncoupling is higher than after 1 h. A reduction cycle at 600 °C after being previously oxidized is also plotted in the graph, showing again similar kinetics as after oxygen uncoupling.

The fact that the reduction kinetics, both at 600 °C and 800 °C, are very much the same after previous oxidation cycles and after different number of oxygen uncoupling cycles where higher amounts of Cu₂O are formed, indicates that the kinetics of Cu₂O are fast enough in comparison to the kinetics of CuO to not influence the reaction rate.

The difference in conversion after 1 h and 15 h of oxygen uncoupling is larger at 600 °C. This can be explained due to the fact that at 800 °C there is more CuO available for reaction because of faster solid diffusion, while at 600 °C the initial amount of CuO available is lower. The higher conversion after longer times of oxygen uncoupling is explained because a higher conversion of CuO has been achieved, so that there is more Cu₂O available that reacts as fast as CuO under these conditions, according to the reaction rates shown in Fig. 9.

When comparing the particle conversion obtained after oxygen uncoupling cycles (Fig. 8) with the particle conversion obtained after regular redox cycles (Fig. 4), one should bear in mind the differences in the time scale of the figures. The regular redox cycles were carried out for 15 min of reduction (Fig. 4), while during the experiments to investigate the influence of the oxygen uncoupling (Fig. 8) the reduction cycle lasted 1 h.

The reaction from CuO to Cu follows the mechanisms indicated in Eqs. (4)–(8) (see Introduction).

The conversion of the oxygen uncoupling is calculated as for the conversion of the reduction reaction (Eq. (10)), taking into account the reaction of the oxygen uncoupling showed in Eq. (9). The maximum weight change (denominator of the Eq. (10)) is now different because the oxygen transport capacity, R_0 , to form Cu₂O is different than to form Cu.

SEM-EDX was carried out for the oxygen uncoupling experiments presented in Table 5 to elucidate whether the CLOU cycles have an influence on the structure of the oxygen carrier. Changes in void fractions and formation of cracks with the number of CLOU cycles were not observed (Fig. 10), as it occurred for the cracks seen for redox-cycled material without CLOU (Fig. 5).

The SEM images indicate that there is no change in the oxygen carrier morphology in terms of cracks and void fractions due to the oxygen uncoupling reaction. To assure that the change in morphology is due to the redox cycles, the same number of CLOU and redox cycles were compared (see Fig. 11).

Fig. 10 shows that SEM images when you increase the number of CLOU cycles do not differ almost one from the other, observing that not bigger cracks are formed when increasing the number of CLOU cycles. However, when the number of redox cycles are increased, the SEM images show an increase in void fractions. From Fig. 11 we can conclude that the redox cycles are responsible of the change in morphology in terms of cracks and void fractions.

Finally, XRD analyses confirmed the presence of Cu₂O after oxygen uncoupling, with higher amounts of Cu₂O when the CLOU was carried out for longer times at higher temperatures, as expected.

4. Conclusions and discussion

This work has investigated the possible causes for the observed sudden drop in reduction rate at higher particle conversions of a CuO/Al₂O₃ oxygen carrier during chemical looping combustion. Thermo-gravimetric analysis was used extensively to measure the redox reaction rates of the oxygen carrier after many consecutive redox cycles at 600 °C and 800 °C. For both temperatures, it was observed that after an initial very fast reaction that lasts for about 20 s, the reaction rate decreases suddenly, and that the cyclic steady state in kinetics was already reached after only a few redox cycles. Several characterization techniques (SEM-EDX, XRD analysis, BET and pycnometer) were used to investigate the particle morphology and chemical composition as a function of the number of redox cycles.

Very large morphological changes have been observed which become more and more pronounced for particles having experienced a larger number of redox cycles, however, the morphological changes did not affect the redox kinetics. An inhomogeneous Cu distribution was observed, but either Cu migration did not occur or it does not affect the kinetics. In addition, it was also shown that CuO has a strong interaction with the Al₂O₃ support, forming CuAl₂O₄ in almost all the possible stages of reaction, including the fresh sample. Despite that the amount of CuAl₂O₄ increased with the number of redox cycles, this did not alter the final conversion, although it can have an influence in the drop of the reaction rate, due to the slower kinetics of CuAl₂O₄ and CuAlO₂ compared to the kinetics of CuO/Cu and Cu₂O/Cu.

The oxygen uncoupling reaction rate was studied to analyse whether the amount of Cu₂O could influence the overall kinetics. Detailed experiments have enabled us to conclude that the redox kinetics are fast enough; when starting the reduction cycle from a considerable amount of Cu₂O after an oxygen uncoupling cycle, it did not affect the reaction rate, although the particle conversion was slightly higher when the initial amount of Cu₂O was higher, which was related to the higher CuO conversion during the longer oxygen uncoupling cycle.

Based on the XRD analysis, it is suggested that after reduction of the accessible copper oxide, CuO, and cuprite, Cu₂O, the remaining CuO and Cu₂O are shielded from reduction during the remaining part of the reduction cycle making it less accessible and causing a drop in reaction rate after a particle conversion because of solid phase diffusion limitations.

This was further corroborated with experiments performed with a copper wire, where it was shown that after 4 h of oxidation still no steady-state was reached.

From the experiments it can be concluded that internal gas phase diffusion limitations cannot be responsible for the sudden decrease in the observed reaction rate, as well as the possible migration of copper from the inside of the particle to the external surface and oxygen uncoupling. By excluding all the above-mentioned phenomena solid phase oxygen diffusion limitations together with the spinel reduction are most likely responsible for the sudden drop in the observed reaction rate at higher particle conversions. This will be studied in more detail in a future work where solid diffusion limitations through oxygen vacancies and the spinel kinetics will be incorporated in a model able to describe the redox kinetics.

Acknowledgements

The research leading to these results has received financial support from Netherlands Organisation for Scientific Research (NWO) (717.013.007) through the ECHO-STIP project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.powtec.2016.06.031>.

References

- [1] J.J. McCarthy, Climate Change, Impacts, Adaptation, and Vulnerability: Contribution of Working Group II to the Third Assessment Report of the Intergovernmental Panel on Climate Change, 2001, <http://books.google.com/books?hl=es&lr=&id=QSoJDCvRXQC&pgis=12001> (accessed March 28, 2014).
- [2] Land Use, Land-use Change, and Forestry: A Special Report of the Intergovernmental Panel on Climate Change, <http://books.google.com/books?hl=es&lr=&id=EyXQW-gRey0C&pgis=12000> (accessed March 28, 2014).
- [3] I.P. on C. Change, Climate Change: The Ipcc Response Strategies (Google eBook), Island Press, 1991 <http://books.google.com/books?id=vKRRIw3Ka6cC&pgis=1> (accessed March 28, 2014).
- [4] N.E.S.R.L. US Department of Commerce, ESRL Global Monitoring Division - Global Greenhouse Gas Reference Network, 2015 (accessed February 19, 2015) <http://www.esrl.noaa.gov/gmd/ccgg/trends/>.
- [5] J. Wilcox, Global Climate and Energy Project, 2014 (accessed March 28, 2014) https://gcep.stanford.edu/pdfs/2wh9Q1Alh3q2zMOQRKD4MQ/JenWilcox_CarbonCapture101_web.pdf.
- [6] J. Davison, Performance and costs of power plants with capture and storage of CO₂, Energy 32 (2007) 1163–1176, <http://dx.doi.org/10.1016/j.energy.2006.07.039>.
- [7] K. Tan, Y. Thambimuthu, OXY-fuel Combustion at the CANMET Vertical Combustor Research Facility - 4b2.pdf, 2014 (accessed March 28, 2014) http://seca.doe.gov/publications/proceedings/01/carbon_seq/4b2.pdf.
- [8] B.J.P. Buhre, L.K. Elliott, C.D. Sheng, R.P. Gupta, T.F. Wall, Oxy-fuel combustion technology for coal-fired power generation, Prog. Energy Combust. Sci. 31 (2005) 283–307, <http://dx.doi.org/10.1016/j.pecs.2005.07.001>.
- [9] F.H. Peron, CO₂ Capture Process Principles and Costs - feron1_vol60n3.pdf, 2014 (accessed March 28, 2014) http://ogst.ifpenergiesnouvelles.fr/articles/ogst/pdf/2005/03/feron1_vol60n3.pdf.
- [10] T. Wall, Y. Liu, C. Spero, L. Elliott, S. Khare, R. Rathnam, et al., An overview on oxyfuel coal combustion—state of the art research and technology development, Chem. Eng. Res. Des. 87 (2009) 1003–1016, <http://dx.doi.org/10.1016/j.cherd.2009.02.005>.
- [11] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, Renew. Sust. Energ. Rev. 39 (2014) 426–443, <http://dx.doi.org/10.1016/j.rser.2014.07.093>.
- [12] M.V. Kathe, A. Empfield, J. Na, E. Blair, L.-S. Fan, Hydrogen production from natural gas using an iron-based chemical looping technology: thermodynamic simulations and process system analysis, Appl. Energy 165 (2016) 183–201, <http://dx.doi.org/10.1016/j.apenergy.2015.11.047>.
- [13] A. Hafizi, M.R. Rahimpour, S. Hassanajili, Hydrogen production via chemical looping steam methane reforming process: effect of cerium and calcium promoters on the performance of Fe₂O₃/Al₂O₃ oxygen carrier, Appl. Energy 165 (2016) 685–694, <http://dx.doi.org/10.1016/j.apenergy.2015.12.100>.
- [14] J. WOLF, M. ANHEDEN, J. YAN, Comparison of nickel- and iron-based oxygen carriers in chemical looping combustion for CO capture in power generation, Fuel 84 (2005) 993–1006, <http://dx.doi.org/10.1016/j.fuel.2004.12.016>.
- [15] S. Noorman, M. van Sint Annaland, Packed bed reactor technology for chemical-looping combustion, Ind. Eng. Chem. Res. 46 (2007) 4212–4220, <http://dx.doi.org/10.1021/ie061178i>.
- [16] V. Spallina, M.C. Romano, P. Chiesa, F. Gallucci, M. van Sint Annaland, G. Lozza, Integration of coal gasification and packed bed CLC for high efficiency and near-zero emission power generation, Int. J. Greenh. Gas Control. 27 (2014) 28–41, <http://dx.doi.org/10.1016/j.ijggc.2014.04.029>.
- [17] H.P. Hamers, F. Gallucci, P.D. Cobden, E. Kimball, M. van Sint Annaland, A novel reactor configuration for packed bed chemical-looping combustion of syngas, Int. J. Greenh. Gas Control. 16 (2013) 1–12, <http://dx.doi.org/10.1016/j.ijggc.2013.02.021>.
- [18] H.P. Hamers, F. Gallucci, P.D. Cobden, E. Kimball, M. van Sint Annaland, CLC in packed beds using syngas and CuO/Al₂O₃: model description and experimental validation, Appl. Energy 119 (2014) 163–172, <http://dx.doi.org/10.1016/j.apenergy.2013.12.053>.
- [19] E.A. Goldstein, R.E. Mitchell, Chemical kinetics of copper oxide reduction with carbon monoxide, Proc. Combust. Inst. 33 (2011) 2803–2810, <http://dx.doi.org/10.1016/j.proci.2010.06.080>.
- [20] A. Abad, J. Adánez, A. Cuadrat, F. García-Labiano, P. Gayán, L.F. de Diego, Kinetics of redox reactions of ilmenite for chemical-looping combustion, Chem. Eng. Sci. 66 (2011) 689–702, <http://dx.doi.org/10.1016/j.ces.2010.11.010>.
- [21] A. Abad, F. García-Labiano, L.F. de Diego, P. Gayán, J. Adánez, Reduction kinetics of Cu-, Ni-, and Fe-based oxygen carriers using syngas (CO + H₂) for chemical-looping combustion, Energy Fuel 21 (2007) 1843–1853, <http://dx.doi.org/10.1021/ef070025k>.
- [22] M.M. Hossain, H.I. de Lasa, Reduction and oxidation kinetics of Co–Ni/Al₂O₃ oxygen carrier involved in a chemical-looping combustion cycles, Chem. Eng. Sci. 65 (2010) 98–106, <http://dx.doi.org/10.1016/j.ces.2009.01.059>.
- [23] J.Y. Kim, J.A. Rodríguez, J.C. Hanson, A.I. Frenkel, P.L. Lee, Reduction of CuO and Cu₂O with H₂: H embedding and kinetic effects in the formation of suboxides, J. Am. Chem. Soc. 125 (2003) 10684–10692, <http://dx.doi.org/10.1021/ja0301673>.
- [24] W. Hu, F. Donat, S.A. Scott, J.S. Dennis, Kinetics of oxygen uncoupling of a copper based oxygen carrier, Appl. Energy 161 (2016) 92–100, <http://dx.doi.org/10.1016/j.apenergy.2015.10.006>.
- [25] L.F. de Diego, P. Gayán, F. García-Labiano, J. Celaya, A. Abad, J. Adánez, Impregnated CuO/Al₂O₃ oxygen carriers for chemical-looping combustion: avoiding fluidized bed agglomeration, Energy Fuel 19 (2005) 1850–1856, <http://dx.doi.org/10.1021/ef050052f>.
- [26] I. Adánez-Rubio, P. Gayán, A. Abad, F. García-Labiano, L.F. de Diego, J. Adánez, Kinetic analysis of a Cu-based oxygen carrier: relevance of temperature and oxygen partial pressure on reduction and oxidation reactions rates in chemical looping with oxygen uncoupling (CLOU), Chem. Eng. J. 256 (2014) 69–84, <http://dx.doi.org/10.1016/j.cej.2014.06.102>.
- [27] H.P. Hamers, F. Gallucci, G. Williams, P.D. Cobden, M. van Sint Annaland, Reactivity of oxygen carriers for chemical-looping combustion in packed bed reactors under pressurized conditions, Energy Fuel 29 (2015) 2656–2663, <http://dx.doi.org/10.1021/ef5027899>.
- [28] M. Wefers, Karl Chankya, Oxides and Hydroxide of Aluminum, 2015 (accessed March 12, 2015) http://www.alcoa.com/global/en/innovation/papers_patents/pdf/TP19_Wefers.pdf.
- [29] T. Mattisson, A. Lyngfelt, H. Leion, Chemical-looping with oxygen uncoupling for combustion of solid fuels, Int. J. Greenh. Gas Control. 3 (2009) 11–19, <http://dx.doi.org/10.1016/j.ijggc.2008.06.002>.
- [30] Y. Wen, Z. Li, L. Xu, N. Cai, Experimental study of natural Cu ore particles as oxygen carriers in chemical looping with oxygen uncoupling (CLOU), Energy Fuel 26 (2012) 3919–3927, <http://dx.doi.org/10.1021/ef300076m>.
- [31] C.K. Clayton, K.J. Whitty, Measurement and modeling of decomposition kinetics for copper oxide-based chemical looping with oxygen uncoupling, Appl. Energy 116 (2014) 416–423, <http://dx.doi.org/10.1016/j.apenergy.2013.10.032>.