Study of the calcination of CaCO_3 by means of a Cu/CuO chemical loop using methane as fuel gas

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Abstract

The Ca-Cu looping process allows a H_2 -rich product gas to be obtained on the basis of the sorption enhanced reforming (SER) concept, while generating a concentrated stream of CO_2 suitable for geological storage or industrial use. Previous works have demonstrated that the Cu/CuO chemical loop provides a feasible alternative for regenerating the CO_2 -sorbent required for the SER with potentially low energy penalties. In this work, the CuO reduction/ CaCO_3 calcination operation, which is the key stage of the Ca-Cu looping process, is experimentally demonstrated in a fixed-bed reactor at TRL4 using pure methane as fuel gas. The effect of the temperature of the solids bed on the operation is also evaluated. A detailed characterization of both CuO- and CaO-based materials resulting from the experiments has been carried out, revealing only minor changes in their textural properties, which demonstrates their high stability after successive oxidation-carbonation-reduction/calcination cycles.

Keywords: chemical looping; CO_2 capture; calcium looping; H_2 production, CaCO_3 calcination;

1. Introduction

There is a need to reduce the emissions of greenhouse gases from industrial processes. It is only by the capture of CO_2 and its subsequent permanent storage that carbon emissions can be drastically reduced far beyond the level currently achievable in large stationary sources [1]. The development of pre-combustion CO_2 capture systems is an attractive option for producing hydrogen with a low-carbon footprint [2]. The global demand for hydrogen is expected to rise in the near future due to the growth in the production of ammonia and methanol, to the increasing use of H_2 in refineries, steel and glass industries and also as a clean fuel in modern gas turbines, combustion engines and fuel cells [3]. Although H_2 can be produced from a wide variety of sources (e.g. natural gas, oil, coal, biomass, electrolysis, solar energy, etc), around 96% of H_2 is currently

obtained from fossil fuels, resulting in the emission of approximately 0.5 Gt CO₂/year into the atmosphere [4].

Steam Methane Reforming (SMR) followed by the water-gas-shift (WGS) operation is the predominant H₂ production technology employed at industrial scale [4, 5]. Around 48% of H₂ is currently obtained by this method [3]. Although SMR is a highly efficient route compared to other alternatives [5], it is an energy-intensive process since a large amount of natural gas needs to be fired in external burners to supply the heat required for the endothermic transformation of methane into H₂ [6, 7]. Moreover, SMR is responsible for significantly high CO₂ emissions (at least 7 kg CO₂ per kg of H₂ produced) [8]. The coupling of SMR with in situ CO₂ separation by using a high-temperature solid sorbent is an attractive option for the sustainable conversion of methane into high-purity H₂ [9, 10]. In the Sorption Enhanced Reforming (SER) process, the combination of a solid sorbent (typically a CaO-based material) with a reforming catalyst favours the production of additional H₂ by removing CO₂ from the gaseous phase [11, 12]. A product gas with more than 90 vol.% of H₂ purity (on a dry basis) and with very low methane and CO contents can be obtained in a single stage under milder conditions (between 600-700 °C) while at the same time the downstream H₂ purification step is significantly simplified [9]. Moreover, the exothermic CO₂ sorption reaction (i. e. the CaO carbonation) provides directly the heat necessary in the reformer for the endothermic reforming reactions to be carried out, so that no additional energy is required to produce the hydrogen [13].

The main challenge for the scaling-up of the SER technology (and in general of any calcium-looping system) is the need to find an energy-efficient procedure for the regeneration of the CaO-based sorbent at a minimum capital cost. The CaO/CaCO₃/CO₂ equilibrium imposes temperatures of around 900 °C to decompose the CaCO₃ under CO₂-rich atmospheres [14]. A large number of process schemes have been reported in the literature for this purpose, but the only one developed to large-pilot scale is the oxy-fuel combustion of additional fuel in a regenerator, originally proposed by Shimizu et al. [15], and subsequently tested up to TRL6-7 for post-combustion applications [16,17]. However, the oxy-combustion concept requires a costly and energy consuming Air Separation Unit (ASU). The use of chemical looping combustion (CLC) systems has been also proposed in an attempt to avoid the need for an ASU and to increase the overall energy efficiency in the calcination of CaCO₃ [18]. The CLC concept is based on

the redox cycling of a metal oxide (oxygen carrier) that is placed in contact with the fuel [19]. The lattice oxygen present in the solid oxidizes the fuel and generates, after the removal of H_2O , a product gas highly concentrated in CO_2 . In a following step, the reduced solid is regenerated when it reacts with air [20]. The separation of CO_2 is inherent to the CLC concept since the dilution of the combustion products with nitrogen from the air is avoided [19]. Some CLC configurations use the sensible heat of oxygen carriers that come from an oxidation reactor at temperatures above $1,000\text{ }^\circ\text{C}$ to supply the heat required for CaCO_3 calcination [21,22]. However, the direct heating through the coupling of endothermic and exothermic reactions in one single stage should result in a higher energy efficiency. General Electric proposed using the heat released from the oxidation of nickel with air to directly calcine CaCO_3 [18]. However, air was used for the oxidation/calcination operation. As a result CO_2 highly diluted with N_2 was generated, and therefore, there is no inherent CO_2 capture in that system.

Abanades et al. [23] first proposed the Ca-Cu looping process to enhance the production of H_2 on the basis of the SER concept. In this process, the heat needed to calcine the Ca-based sorbent comes from the exothermic reduction of CuO with a gaseous fuel, which produces an easily-separable stream of CO_2 . The basic scheme of the Ca-Cu looping process consists of a sequence of three reaction steps, as depicted in Fig. 1 [24]. The first stage involves the SER of methane to produce a H_2 -rich gas [25]. In the second stage, the Cu-based material is oxidized with air. As this reaction is highly exothermic, the operating temperature needs to be controlled to avoid the decomposition of CaCO_3 through partial calcination. A low oxygen content in the feed, achieved by recycling a large fraction of the product gas (which is virtually pure N_2) and a low temperature operation (i. e. in the solids bed and in the gaseous feed) are the conditions required to limit the increase in temperature in the oxidation front [26]. In the third stage, a suitable CuO/CaCO_3 molar ratio in the reactor (which depends on the composition of the reducing gas) is required to ensure that the heat released from the reduction of CuO is sufficient to completely decompose the CaCO_3 formed during the SER without the need for an external energy supply [27]. The operation needs to be carried out at atmospheric pressure to facilitate the calcination at temperatures of around $900\text{ }^\circ\text{C}$, which reduces the energy demand of the process and avoids the sintering of solids [27].

Significant progress has been made in recent years in the development of the Ca-Cu looping process [28]. Elaborate reactor models, similar to those used in fixed-bed CLC

systems [29, 30], have been developed to describe accurately the temperature and gas composition profiles at every stage of the Ca-Cu process [25-27, 31-33]. With these results, new operating strategies have been devised in order to reduce the number of reactors required, increase the CO₂ capture efficiency and avoid possible side reactions that could destabilize the process performance [34-36]. The thermal integration of the Ca-Cu looping process on a large scale has been also evaluated [37, 38], obtaining high CO₂ capture efficiencies with moderate efficiency penalties compared to benchmarking systems without CCS. Moreover, a good number of studies have recently been published on high-performance materials with direct application to the Ca-Cu looping process. Combined reforming catalyst/CaO solids have been synthesized to reduce diffusional resistances between particles and minimize the amount of inert during the SER operation [39-41]. CaO-CuO composites obtained from very different synthesis routes have shown almost total CuO/Cu conversions and stable CO₂ carrying capacities of more than 0.3 g CO₂/g of solids after multicycle operation carried out in TGA and micro fixed-bed reactors [42-45].

The experimental viability of the main reaction stages of the Ca-Cu looping process has been demonstrated in lab-scale fixed-bed reactors within the framework of the ASCENT project [46]. Grasa et al. [47] studied the SER operation at different pressures using a mixture of a commercial reforming catalyst and a calcium-based sorbent. Both materials exhibited excellent performances after repetitive oxidation-reduction-reforming cycles. Alarcón et al. [48] showed that the dilution of the O₂ in the feed by simulating the recirculation of a large part of the product gas (virtually pure N₂) allows the maximum temperature achieved during the Cu oxidation to be kept below 800 °C, which would minimize the calcination of the Ca-based sorbent during the operation. Finally, the calcination of CaCO₃ by means of the in situ CuO reduction was also studied using mixtures of H₂ and CO as fuel gas [48, 49].

In this work, the CuO reduction/CaCO₃ calcination stage carried out with only methane is demonstrated under pseudo-adiabatic conditions in a fixed-bed reactor at TRL4. To our knowledge, no such study has yet been reported in the literature. The effect of the temperature of the solids bed on the operation is also assessed. A detailed characterization of the functional materials resulting from the test has been carried out in order to evaluate possible changes in the structure of the solids after multiple redox and carbonation/calcination cycles.

2. Material and methods

The reduction/calcination experiments were conducted in a fixed-bed reactor consisting of about 1 m-long tube made of Inconel with an inner diameter of 38 mm (OD=42 mm). In a typical experiment, the reactor was loaded with 1060 g of a homogeneous mixture of a copper-based catalyst (60 wt% Cu supported over silica) and a calcined CaO-based solid (99 wt% CaO). These materials were supplied by Johnson Matthey and Carmeuse, respectively. The solids were crashed and sieved to obtain a particle diameter of about 3 mm. A multipoint K-type thermocouple (14 points) was used to measure the axial temperature profiles. The reactor was covered with about 100 mm wide layer of quartz wool to minimize the loss of heat. Both the reactor and the insulating material were placed in a ceramic furnace. The experiments were carried out at atmospheric pressure. The gaseous feeds ~~was~~ were preheated by means of two heating tapes (up to 400° and 620 °C for the carbonation and the reduction/calcination step, respectively). The gas flow rates were regulated using mass flow controllers (of up to 5 Nl/min and 10 Nl/min of CH₄ and CO₂, respectively). The product gas was cooled and subsequently dried by means of a silica bed located before the analyzers. The composition of the gas was measured online using an analyzer equipped with infrared and thermal conductivity detectors. The solids were previously heated at temperatures between 550 °C and 820 °C to evaluate the effect of the initial temperature of the bed on the reduction/calcination operation. During the experimental campaign, the CuO- and CaO-based materials were subjected up to 15 reduction/calcination-oxidation-carbonation cycles. The fixed-bed reaction system is represented in Fig. 2.

X-ray diffraction (XRD) analyses were performed to identify the main crystalline phases present in the CuO-based material after multiple cycles. A Siemens D500/501 powder diffractometer equipped with a Cu K α monochromatic X-ray tube was used. Diffraction data were collected over a 2 θ scan range from 20° to 70° using a step size of 0.025° and a scan time per step of 1 s. The surface morphology of the solids was investigated using a Quanta FEG 650 scanning electron microscope (SEM), equipped with an energy-dispersive X-Ray (EDX) analyser (Ametek-EDAX fitted with an Apollo X detector). The specific Brunauer-Emmet-Teller (BET) surface area and pore volume of the materials were determined from N₂ adsorption/desorption isotherms obtained at approximately -196°C using a Micromeritics ASAP 2460 after out-gassing the samples under vacuum for 6 h at 200 °C.

3. Results and discussion

Fig. 3 shows SEM images of both CuO- and CaO-based materials before and after 15 ~~several~~ oxidation-carbonation-reduction/calcination cycles. The fresh CuO-based sample (Fig. 3a) has a high porosity and contains large grains enriched in CuO. The morphology of the used CuO-based catalyst (Fig. 3b) is similar to that seen in the fresh sample and there is hardly any sign of sintering. The back scattered electrons (BSE) technique ~~(not included here for the sake of simplicity)~~ presents the denser CuO phase in a light grey colour, which is well dispersed over a SiO₂ support of lower density, shown in dark grey (Fig. 3c and Fig. 3d). ~~The morphology of the used CuO-based catalyst (Fig. 3b) is similar to that seen in the fresh sample and there is hardly any sign of sintering.~~ Moreover, SEM-EDX analyses reveal that small amounts of Ca compounds are present in the cycled CuO-based sample. The morphology of the fresh CaO-based material is represented in Fig. 3e. The sample has a very low porosity and larger grains. After the multicycle operation, a certain degree of sintering is observed in the CaO-based solid (Fig. 3f). SEM-EDX reveals the presence of Cu in cycled CaO-based samples.

The BET pore surface area, pore volume and average pore size of the tested materials are listed in Table 1. The BET surface area of the fresh CuO-based catalyst is 158 m²/g and the pore volume is 0.27 cm³/g, which are significantly higher than the values reported for other materials with high CuO contents [50,51]. The average pore size obtained from the BJH pore volume distribution of this material is 3.1 nm. Small changes can be observed in the textural properties of the used CuO-based catalyst, which confirms the high stability of this material after successive redox cycles. The BET surface area of the fresh CaO-based sample is considerably lower (i.e., 10.8 m²/g), although it is within the range typically reported for calcium-based sorbents [43]. Both the pore volume and average pore size are also lower than those of the CuO catalyst (i.e., 0.02 cm³/g and 1.6 nm, respectively). However, the textural properties of the used CaO-based sample remain unaltered and do not show any significant variations after the experimental tests.

Table 1. BET pore surface area, pore volume and average pore size of the fresh and used CuO- and CaO-based materials.

<u>Sample name</u>	BET area	BJH pore	Average
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		volume	pore size
	(m ² /g)	(cm ³ /g)	(nm)
Fresh Cu-based solid	158	0.27	3.1
Cycled Cu-based solid	135	0.21	2.8
Fresh Ca-based solid	10.8	0.02	1.6
Cycled Ca-based solid	8.9	0.01	1.5

Fig. 4 represents the XRD analysis of a sample of CuO-based catalyst after 15 multiple oxidation-carbonation-reduction/calcination cycles. As expected, the most prominent compounds in the diffractogram are CuO and SiO₂. Despite working at temperatures of around 900 °C, there is an absence of Cu₂O. However, a small amount of mixed Ca-Cu oxides can be observed, in agreement with the results of previous works [43,48]. These combined oxides could form carbonates, which would affect the CO₂ sorption capacity of the solids would be affected. However, the study of this modification is out of the scope of this work.

Previous heat-transfer experiments without any chemical reaction allowed the overall heat transfer coefficient to be estimated. A value of about 5 W/m²K was calculated, which demonstrates that the system operates relatively close to adiabatic conditions. To study the calcination of CaCO₃ by the simultaneous reduction of CuO with methane, the reactor was first heated up in air to obtain a solids temperature profile of between 550 and 700 °C. Then, a flow of 5 NI/min of pure CO₂ preheated to 400 °C was introduced into the fixed bed for 30 min to carry out the partial carbonation of the CaO-based particles. According to the TGA analysis carried out in a previous work [48], after this period of time, the reactor should contain about 10.5 wt.% of CaCO₃ together with 26.4 wt% of CuO. The rest of the bed was mainly inert CaO and inert support of the CuO-based catalyst (i.e, SiO₂). This means that a Cu/Ca molar ratio of around 3.1 was present in the bed, which is the composition needed to theoretically reach neutral conditions in the reaction fronts during the reduction/calcination operation with CH₄ [27]. During the carbonation, the solids bed was progressively heated until a temperature profile of between 620 °C at the bottom and nearly 800 °C at the top was obtained. For the reduction of CuO, a flow rate of 3 NI/min (100 % CH₄) preheated to 620 °C was used. The evolution of the temperature and gas composition during the operation is represented in Fig. 5.

Once the fuel gas has been fed into the fixed bed, the temperature of the solids rapidly increases because of the exothermic reduction of the CuO particles even at low starting temperatures. During the first minutes ($t < 3$ min), the temperature achieved in the reduction front is lower than 800 °C. In these conditions, the calcination of CaCO₃ is impeded, and therefore, during this period of time, the CO₂ present in the product gas comes exclusively from the oxidation of CH₄. Because of the low content of CuO in the bed and the high concentration of CH₄ in the feed, the reduction front advances faster than the heat exchange front resulting from the reduction of CuO. Consequently, the reduced solids are left behind at a high temperature, so that the fuel gas arrives at the reduction front already preheated by these solids. As the reduction front moves forward, the temperature profile progressively increases until it reaches a maximum of around 900 °C ($t > 4$ min). At this temperature, CaCO₃ is rapidly calcined, resulting in increasing quantities of CO₂ in the product gas of up to 92 vol % (on a dry basis). From $t = 2$ min to $t = 4$ min, the conversion of CH₄ is almost completely achieved. From that point onwards, the CH₄ in the product gas progressively rises during a long breakthrough period (until $t < 25$ min), which demonstrates that the reactivity of CH₄ with CuO is significantly lower than that of H₂ and CO with the same oxygen carrier (as described in [48,49]). A small amount of CO (i.e., below 3 vol.%) is present in the product gas during the first minutes of the breakthrough period. This is because the high temperatures and high CO₂ content in the atmosphere favour both the steam methane reforming (SMR) and the reverse water gas shift (RWGS) reactions catalyzed by the Cu-based particles. As the copper-based particles approach total reduction and the temperature of the bed decreases, the content of CO in the product gas increases until it reaches a stationary value of about 10 vol.%, which is maintained throughout the post-breakthrough period.

To initiate a new cycle, diluted air was fed into the reactor to oxidize the Cu particles at temperatures below 850°C. Additional experiments were carried out to evaluate the effect of the initial temperature of the solids bed on the reduction/calcination operation with methane in the feed. These tests were carried out with initial average temperatures from 700 °C to 780 °C, assuming the operating conditions of the experiment described above. As shown in Fig. 6, the temperature and composition profiles formed during the experiments changed significantly. At an average starting temperature of about 700 °C in the bed, the reduction of CuO with methane is not favoured and the increase in the

temperature profile during the operation is low. As a result of that, there are no temperatures above 820 °C in any part of the bed during the reduction/calcination test. In these conditions, CaCO_3 calcination is hampered, and consequently, the CO_2 detected in the product gas must mainly come from the oxidation of methane. Despite the low inlet flow of methane (i.e., 3 Nl/min) a large fraction of the fuel gas is not converted during the pre-breakthrough period and from the very beginning of the test concentrations of CH_4 in the product gas higher than 20 vol.% are detected. From $t=3$ min onwards, the presence of CH_4 in the product gas progressively increases up to a stable value of around 80 vol.% after 18 minutes of operation. The low temperatures of the temperature profile do not favour both the SMR and the reverse water-gas-shift reactions and so concentrations of CO lower than 1 vol.% are obtained during the experiment.

Higher starting temperatures in the bed allow faster reduction of CuO with methane, and as a result of that, a greater increase in the temperature profiles can be observed, especially in the second half of the reactor. At an average starting temperature in the bed of about 780 °C, the almost complete conversion of CH_4 is achieved during the first minutes and the pre-breakthrough period is extended up to 4 minutes. Temperatures higher than 900 °C are achieved in these conditions, which should lead to the total calcination of the second part of the bed. Almost completely pure CO_2 (on a dry basis) is obtained as product gas during the first 6-7 minutes of operation. From that point onwards, the concentration of CH_4 , CO and H_2 increases (breakthrough curve) due to the copper-based particles approach their total reduction and to the steam reforming and WGS reactions, respectively.

In the subsequent Cu oxidation step, which is required for a multicycle operation, the CO_2 measured in the product gas indicates approximately the degree of calcination achieved in the previous reduction/calcination stage. For the conditions of the base case represented in Fig. 5, about 50% of the initial CaCO_3 present in the bed is calcined. That means about 1.07 moles CH_4 (i.e., 3 Nl/min during 8 min) are needed to calcine about 0.56 moles CaCO_3 . In the experiment carried out at the highest initial bed temperature (Fig. 6d), the amount of CO_2 measured during the subsequent Cu oxidation corresponds to about 60% of CaCO_3 calcination. In this case, about 1.07 moles CH_4 calcine around 0.67 moles CaCO_3 .

Conclusions

The CuO reduction/CaCO₃ calcination operation (i.e., the key reaction stage of the Ca-Cu looping process) has been studied using commercial CaO- and CuO-based materials and pure methane as fuel gas. The feasibility of this stage has been demonstrated under pseudo-adiabatic conditions in a fixed-bed reactor at TRL4. With starting temperatures in the solids bed higher than 740 °C and by feeding in 3 Nl/min of methane, it was possible to oxidize completely the fuel gas and calcine part of the CaCO₃ particles of the bed. During the pre-breakthrough period, almost pure CO₂ (after H₂O removal) was obtained as product gas. The copper-based material was able to catalyse both the SMR and RWGS reactions, which were favoured by the high temperatures and the high content of CO₂ in the atmosphere. As a result, significant amounts of CO and H₂ were detected in the product gas as the CuO particles approached total reduction. The relatively long breakthrough curves observed in the experiments demonstrated that the reactivity of CH₄ with CuO is significantly lower than that of H₂ and CO. Higher starting temperatures in the bed enhanced CH₄ oxidation and extended the duration of the pre-breakthrough period. Under these conditions, temperatures above 900 °C were achieved and the CO₂ resulting from the calcination of CaCO₃ increased in the product gas. Moreover, both the SMR and RWG reactions were highly favoured and increasing amounts of CO and H₂ were measured at the reactor exit. With the help of the SEM, N₂ adsorption and XRD techniques, a detailed characterization of both commercial CaO- and CuO-based materials was carried out. Only minor changes were observed in the textural properties of the materials before and after the multicycle operation, which is proof of their high stability. The operation at high temperature slightly modified the chemical composition of the materials and combined copper-calcium oxides were detected, which could lead to the formation of carbonates in the presence of CO₂.

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Figure captions.

Fig. 1. Main reaction stages involved in the Ca-Cu looping process carried out in fixed-bed reactors.

Fig. 2. Schematic diagram of the fixed-bed reactor system for the reduction/calcination operation.

Fig. 3. SEM images of the functional materials used in the reduction/calcination study: a) SE-SEM fresh CuO-based catalyst, b) SE-SEM used CuO-based catalyst, c) BSE-SEM fresh CuO-based catalyst, d) BSE-SEM used CuO-based catalyst, e) fresh CaO-based material, f) used CaO-based material.

Fig. 4. XRD pattern of the CuO-based catalyst after ~~several~~ 15 oxidation-carbonation-reduction/calcination cycles ~~tests~~.

Fig. 5. Axial temperature profiles and outlet gas composition during the CuO reduction/CaCO₃ calcination operation with methane.

Fig. 6. Effect of the starting temperature on the temperature and gas composition profiles during the CuO reduction/CaCO₃ calcination operation with methane. In Fig. 6a, dots and lines represent the temperature profiles after 4 and 10 minutes of operation, respectively. Data in white correspond to initial average temperature in the bed of 700 °C, data in grey to 740 °C and data in black to 780 °C.