

# Self-activated, Nanostructured Composite for Improved CaL-CLC technology

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## Abstract

The development of bifunctional CaO/CuO matrix composites with both high and stable reactivity is a research priority and key for the development of calcium looping integrated with chemical looping combustion (CaL-CLC), a new CO<sub>2</sub> capture technology that eliminates the requirement for pure O<sub>2</sub> for the regeneration of CaO-based sorbents. In this work, a simple but effective approach was first used, i.e., solution combustion synthesis (SCS), to produce various nanostructured CaO/CuO matrix composites with homogenous elemental distributions. All CaO/CuO matrix composites possessed increased CO<sub>2</sub> uptake in the form of self-activation and excellent cyclically stable O<sub>2</sub> carrying capacity over as many as 40 reaction cycles. For instance, the final carbonation conversion of CaO-CuO-1-800-30 was 51.3%, approximately 52.7% higher than that of the original material (33.6%). Here, the self-activation phenomenon have been observed for the first time in contrast to the rapid decay in CO<sub>2</sub> uptake capacity previously reported, due mainly to the increase of both specific surface area and pore volume. In-situ X-ray diffraction (in-situ XRD) analysis revealed that no side reactions occurred between CaO/CaCO<sub>3</sub> and CuO/Cu during the overall process. All of these results make CaO/CuO matrix composites an attractive candidate for CaL-CLC.

**Keywords:** Calcium looping process; carbon capture; solution combustion synthesis; bifunctional composite; in-situ XRD; self-activation.

## 1. Introduction

The calcium looping process (CaL) is one of the most promising CO<sub>2</sub> capture technology because it uses abundant and cheap CaO-based materials as sorbent precursors with a high theoretical sorption capacity (i.e., 0.786 g CO<sub>2</sub> per g CaO) [1-3]. This process exploits a reversible gas-solid reaction between CaO and CO<sub>2</sub> to form CaCO<sub>3</sub>, according to Eq. (1), and is

implemented practically in interconnected carbonation and calcination reactors, respectively, as shown in Fig. 1. In order to avoid dilution of the CO<sub>2</sub> with N<sub>2</sub> in the calcination reactor, fuel is burned in pure O<sub>2</sub> derived from an air separation unit (ASU) to provide heat required for the calcination of CaCO<sub>3</sub>, with all CO<sub>2</sub> produced being captured [4,5].

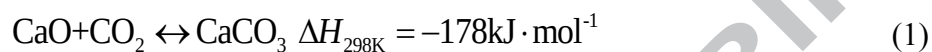
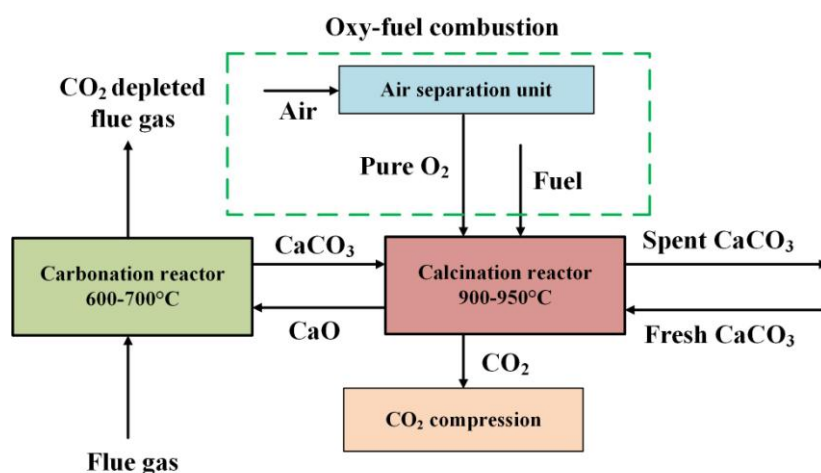


**Fig. 1.** Schematic diagram of CaL process.

Recently, CaL integrated with chemical looping combustion (CaL-CLC), a modification of CaL process, has been proposed to reduce the power consumption associated with the ASU, thereby further lowering the energy penalty [6,7]. Work by Ozcan et al. [8] showed that compared to the energy penalty of 7.2% for a conventional CaL configuration, the CaL-CLC process achieved a significantly reduced energy penalty of 3.5% with the same overall CO<sub>2</sub> capture efficiency (~90%), due mainly to the absence of the ASU. The core idea of the modification lies in the possibility that an exothermic reduction of CuO with reducing gaseous fuel, such as CH<sub>4</sub>, H<sub>2</sub>, CO and syngas, can supply the heat required to calcine CaCO<sub>3</sub> by means

of bifunctional CaO/CuO matrix composites, according to Eqs. (2)-(4), as illustrated in Fig. 2 [9].

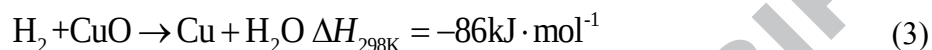
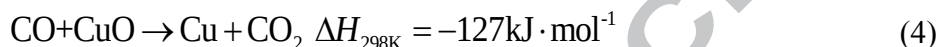
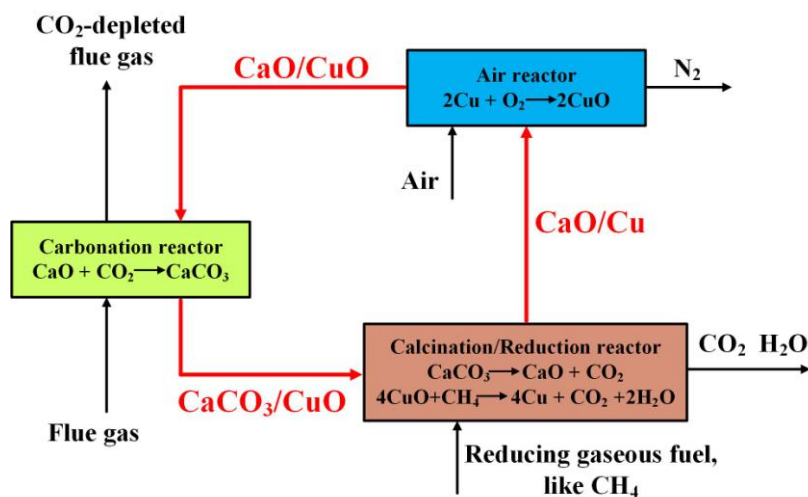


**Fig. 2.** Schematic diagram of CaL-CLC process.

However, because the composite material consists mainly of CaCO<sub>3</sub> and CuO/Cu, both of which possess low Tammann temperatures (533°C [3] and 527°C/405°C [10], respectively), CaL-CLC faces severe challenges from a material point of view. During the repeated carbonation/calcination and redox reactions, significant changes occur in the molar volume of the composites, thus posing a significant challenge in terms of reducing the surface area, pore volume and mechanical integrity of the composite material. The loss of surface area and pore volume eventually leads to a decline in CO<sub>2</sub> uptake and O<sub>2</sub> carrying capacity.

On the basis of previous work [11-15], it can be concluded that, while the O<sub>2</sub> carrying capacity of CaO/CuO matrix composites is usually stable compared to the CO<sub>2</sub> uptake capacity, the rapid decay in CO<sub>2</sub> uptake capacity is a serious problem for CaL-CLC that urgently needs to be solved. It is well known that synthesis methods play a critical role in the physicochemical properties of the resulting materials, including crystallite size, specific surface area, redox ability, and sorption capacity [16]. Hence, major efforts to date have been devoted to preparing CaO/CuO matrix composites using different synthesis methods [12]. Table 1 summaries the CO<sub>2</sub> capture performance of bifunctional CaO/CuO matrix composites prepared via different synthesis methods, which was carried out in thermogravimetric analyzer (TGA) or fixed bed reactor (FBR). The carbonation conversion of CaO/CuO matrix composites, which was prepared by wet granulation method, wet mixing, or co-precipitation, decreased at least 20% after only few cycles. In spite of CaO/CuO matrix composites synthesized via the sol-gel approach exhibited stable CO<sub>2</sub> uptake capacity, the procedure of the sol-gel method is relatively complex, time-consuming and probably prohibitively expensive. Therefore, a simple but effective synthesis approach for the scalable production of highly efficient CaO/CuO matrix composites remains a research priority.

**Table 1.** Summaries of CO<sub>2</sub> capture performance of bifunctional CaO/CuO matrix composites prepared by different synthesis method

| Authors             | Synthesis method | CaO/CuO molar ratio | Number of cycles | CO <sub>2</sub> uptake capacity (%) |       |
|---------------------|------------------|---------------------|------------------|-------------------------------------|-------|
|                     |                  |                     |                  | Initial                             | Final |
| Manovic et al. [13] | wet granulation  | 1.43                | 3                | 65.1                                | 37.2  |
| Recio et al. [10]   | wet granulation  | 1.14                | 16               | 17                                  | 8     |

|                         |                  |      |    |      |      |
|-------------------------|------------------|------|----|------|------|
| Ridha et al. [17]       | wet granulation  | 3.16 | 12 | 32.1 | 19   |
| Qin et al. [14]         | wet mixing       | 0.25 | 4  | 17.4 | 13.4 |
| Kierzkowska et al. [18] | co-precipitation | 1    | 15 | 83.5 | 55.6 |
| Kierzkowska et al. [11] | sol-gel          | 0.77 | 15 | 51   | 52   |

An alternative approach for producing CaO/CuO matrix composite is solution combustion synthesis (SCS), which has been considered a time- and energy-saving method for the large-scale synthesis of a variety of advanced nanomaterials with high purity [19], including composites [20,21] and catalysts [22,23]. SCS is characterized by a rapid (typically from 0.1 to 10 cm·s<sup>-1</sup>) high-temperature (1000-3000°C) self-sustaining reaction wave that propagates through the solution after the initial exothermic reaction mixture has been ignited by means of an external thermal source (the ignition time is of the order of a few seconds) [24]. The final products are thus formed without any additional energy input and are obtained within a shorter time (once the mixed solution is prepared) compared to that needed for conventional synthesis methods such as sol-gel and co-precipitation. Moreover, an additional step, i.e., the high-temperature product calcination that typically follows the conventional synthesis method, can be eliminated via SCS [25]. Li et al. [26-29] confirmed good and cyclically stable CO<sub>2</sub> capture performance of CaO-based sorbents synthesized via SCS. Furthermore, it has been reported that a high and stable CO<sub>2</sub> uptake capacity can be obtained for nanostructured CaO-based sorbents [3,30,31]. Hence, the development of nanostructured CaO/CuO matrix composites may possess the potential to deal with the problem of a rapidly decaying CO<sub>2</sub> uptake capacity of CaO/CuO matrix composites for CaL-CLC.

Recently, an interesting phenomenon known as self-activation, i.e., an increase of CO<sub>2</sub> uptake capacity during cycling, has been reported mainly for thermally-pretreated CaO-based sorbents in the CaL process [32-34]. This phenomenon can be explained by the formation of a hard and stable skeleton during thermal pretreatment, whereby solid-state diffusion carbonation is enhanced in the first carbonation/calcination cycle. A quick calcination following an enhanced diffusive carbonation stage results in a renovated porous skeleton with increased surface area for the next carbonation, subsequently leading to an increase in CO<sub>2</sub> uptake capacity [35,36]. For instance, Manovic and Anthony [32] found that, after grinding and pretreatment at temperatures of 1000-1200°C, carbonation conversions of four Canadian limestones increased with the cycle number, reaching a carbonation conversion of 50% in the 30<sup>th</sup> cycle. Moreover, Chen et al. [37] demonstrated that the beneficial influence of self-activation could be retained for over 1000 cycles. Therefore, if self-activation of CaO/CuO matrix composites could take place in the CaL-CLC process, the generic problem of a decreasing CO<sub>2</sub> uptake capacity would be largely resolved.

In this work, this simple but effective approach, i.e., SCS, was first utilized to synthesize various nanostructured CaO/CuO matrix composites without any inert support material. The cyclic CO<sub>2</sub> uptake capacity and redox characteristics of the synthesized composites were evaluated. The results obtained in this work indicated that self-activation of CaO/CuO matrix composites had occurred over the repeated cycles, due mainly to the increase of both specific surface area and pore volume, which was verified by N<sub>2</sub> adsorption measurements. In addition, the evolution of phase compositions during the overall CaL-CLC process was analyzed using in-situ X-ray diffraction (in-situ XRD). The results confirmed that no side reactions occurred between the CaO/CaCO<sub>3</sub> and Cu/CuO, and the phase Ca<sub>2</sub>CuO<sub>3</sub> initially formed during the preparation was also an active component for CO<sub>2</sub> capture.

## 2. Experimental Section

### 2.1. Materials and Sorbent preparation

Here,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were used as calcium precursor and copper precursor, respectively. Ethanol was selected as the fuel for SCS.

The preparation procedure using SCS is shown schematically in Fig. 3. For the production of 0.5 g of bifunctional CaO/CuO matrix composites, predetermined amounts of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were added to deionized water in a 50 mL beaker. The mixed solution was continuously stirred (1000 rpm) for 20 min at 30°C in an electrically heated thermostat water bath to form a homogeneous system. Subsequently, 50 mL ethanol was added to the solution, followed by stirring for another 3 min. Next, the homogeneously mixed solution was placed into a muffle furnace for combustion at 800-850°C under air for 30-120 min. After combustion, the residue was ground to a fine powder in an agate mortar. Here, the molar ratios of CaO (derived from  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) to CuO (derived from  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) were specified as 3, 2, 1 and 0.5. Pure CuO was also prepared according to the same procedure without the addition of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and used as a reference material.

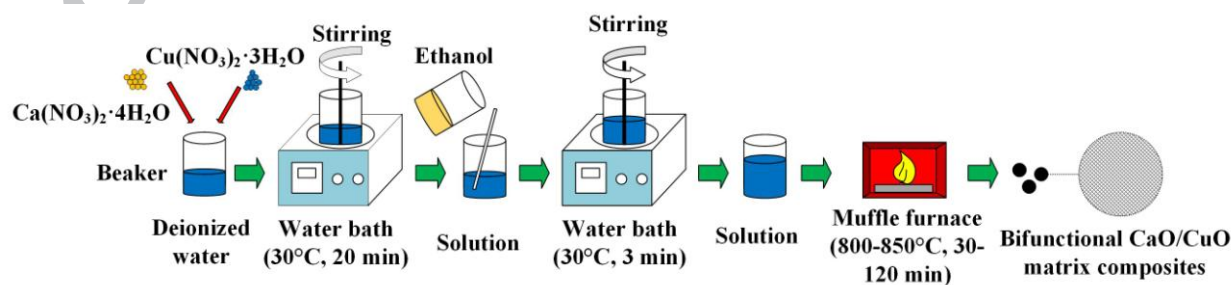


**Fig. 3.** Preparation procedures of CaO/CuO matrix composites via SCS.

For simplicity, the abbreviation CaO-CuO-x-T-t is used to denote the different CaO/CuO matrix composites, where x represents the molar ratio of CaO to CuO, T is the combustion temperature (°C), and t is the combustion duration (min). Here, the abbreviation CuO\* is used for the pure CuO sorbent, which is synthesized at a combustion temperature of 800°C for a duration of 30 min.

## 2.2. Material characterization

A particle size analyzer (S3500, Microtrac, USA) was used to measure the particle size distributions of the as-synthesized sorbents. An ambient X-ray powder diffraction unit (ex-situ XRD, SmartLab, Japan) was used to detect the crystalline phase of synthetic sorbents, using Cu K $\alpha$  radiation in a 2 $\theta$  range of 10°-80° with an accelerating voltage of 45 kV and a tube current of 40 mA. In addition, the evolution of phase compositions during the cyclic carbonation/calcination and redox reactions of the CaO/CuO matrix composites was investigated via in-situ X-ray powder diffraction (PANalytical Empyrean diffractometer equipped with an Anton Paar XRK 900 high-temperature chamber). Details of the reaction conditions used in the in-situ experiments are available in Supplementary Tables S1, S2 and Figure S1.

The apparent morphologies of the sorbents were analyzed by scanning electron microscopy (SEM, Hitachi S-4800, Japan) equipped with an energy dispersive X-ray spectrometer (EDX, NORAN System 7, USA), which enabled the analysis of elemental composition and dispersion determination on the surface. Transmission electron microscopy (TEM, Hitachi HT7700, Japan) was used to observe the crystal morphology of the sorbents. The specific surface area and pore volume of the sorbents before and after cyclic experiments were determined by the Brunauer-

Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method using a N<sub>2</sub> adsorption measurement (Belsorp mini II, Microtrac-BEL, Japan).

### 2.3. Measurement of cyclic reactivity

The cyclic carbonation/calcination and redox process was carried out in a thermogravimetric analyzer (TGA, STA449F3, NETZSCH, Germany). Typically, about 20 mg of sample was dispersed on a quartz pan to investigate its CO<sub>2</sub> uptake and/or O<sub>2</sub> carrying capacity. The cyclic testing conditions for CaO/CuO matrix composites were as follows: the calcination/reduction step was performed for 15 min in an atmosphere of 15 vol% CH<sub>4</sub> (N<sub>2</sub> balance, a total volume flow of 300 mL·min<sup>-1</sup>) while the TGA was heating from 650 to 800°C. The oxidation step was carried out at 650°C for 20 min in an atmosphere of 21 vol% O<sub>2</sub> (N<sub>2</sub> balance, a total volume flow of 300 mL·min<sup>-1</sup>), and the carbonation step was conducted at the same temperature for 30 min in an atmosphere of 15 vol% CO<sub>2</sub> (N<sub>2</sub> balance, a total volume flow of 300 mL·min<sup>-1</sup>). The initial heating step (i.e., from room temperature to 650°C) and all cooling steps of the experiments were performed in a N<sub>2</sub> flow (300 mL·min<sup>-1</sup> at a heating/cooling rate of 10°C·min<sup>-1</sup>). The rationale for the experimental design of the TGA studies is discussed and the experimental conditions of the TGA studies concerning CaO/CuO matrix composites are summarized in Supplementary Table S3. For CuO\*, the carbonation step was not included in the experiments, and the conditions of reduction/oxidation reactions were the same as for the CaO/CuO matrix composites. The calcination/carbonation and/or redox reactions were repeated for a specified number of times. During the TGA testing, sample mass was monitored and recorded as a function of time. CO<sub>2</sub> uptake and/or O<sub>2</sub> carrying capacity was then calculated based on the measured mass change, assuming that mass change was caused only by the formation/decomposition of CaCO<sub>3</sub> and the reduction/oxidation of CuO/Cu.

In this work, carbonation conversion  $C_{N,\%}$  and oxidation conversion  $O_{N,\%}$  were used to characterize the  $\text{CO}_2$  uptake and  $\text{O}_2$  carrying capacity of the sorbent, respectively, as follows:

$$O_{N,\%} = \frac{m_{N,\text{oxi}} - m_{N,\text{cal/red}}}{m_0 \cdot \varphi_{\text{CuO}}} \cdot \frac{M_{\text{Cu}}}{M_{\text{O}}} \cdot 100\% \quad (5)$$

$$C_{N,\%} = \frac{m_{N,\text{car}} - m_{N,\text{oxi}}}{m_0 \cdot \varphi_{\text{CaO}}} \cdot \frac{M_{\text{CaO}}}{M_{\text{CO}_2}} \cdot 100\% \quad (6)$$

where  $C_{N,\%}$  (in %) means the carbonation conversion of the sample in the  $N^{\text{th}}$  cycle, indicating the fractional conversion of CaO, derived from the sample, to  $\text{CaCO}_3$ ;  $m_0$  (in g) represents the mass of the initial sample;  $\varphi_{\text{CaO}}$  (in wt%) denotes the CaO content in the as-synthesized sample;  $m_{N,\text{car}}$  and  $m_{N,\text{oxi}}$  (in g) are the mass of the sample after the  $N^{\text{th}}$  carbonation and oxidation, respectively; and  $M_{\text{CaO}}$  and  $M_{\text{CO}_2}$  (in  $\text{g} \cdot \text{mol}^{-1}$ ) are the molar mass of CaO and  $\text{CO}_2$ , respectively.  $O_{N,\%}$  (in %) means oxidation conversion of the sample to CuO in the  $N^{\text{th}}$  cycle, indicating the fractional conversion of Cu, derived from the sample.  $\varphi_{\text{CuO}}$  (in wt%) denotes CuO content in the as-synthesized sample;  $m_{N,\text{oxi}}$  and  $m_{N,\text{cal/red}}$  (in g) are the mass of the sample after the  $N^{\text{th}}$  oxidation and calcination/reduction, respectively; and  $M_{\text{Cu}}$  and  $M_{\text{O}}$  (in  $\text{g} \cdot \text{mol}^{-1}$ ) are the molar mass of Cu and O, respectively.

### 3. Results and discussion

#### 3.1. Effect of combustion temperature and duration

Fig. 4 represents the  $\text{CO}_2$  uptake capacity of CaO-CuO-1 synthesized under various combustion temperatures and durations. An increase in both combustion temperature and

duration resulted in a clear decrease in CO<sub>2</sub> uptake capacity of the CaO/CuO matrix composites. Moreover, as compared to duration, combustion temperature played a more critical role in determining CO<sub>2</sub> uptake capacity. These results can be explained based on the fact that high temperatures and long durations aggravate the sintering of CaCO<sub>3</sub> and CuO/Cu in CaO/CuO matrix composites, which leads to the destruction of the porous structures of the composites [27]. Importantly, an increase of CO<sub>2</sub> uptake capacity with repeated cycles (i.e., self-activation [32,33,36]) can be observed during three calcination/reduction, oxidation and carbonation cycles. This phenomenon is surprising, since a rapid decline in CO<sub>2</sub> uptake capacity of CaO/CuO matrix composites rather than an increase has always been reported in previous work [10-15,17,18]. The self-activation of CaO/CuO matrix composites without any inert support observed here is a highly practical and valuable result, since it can significantly extend the lifetime of composites in the CaL-CLC process, thus reducing the amount of fresh composite makeup required to replace the spent material and resulting in a substantial improvement in the economics of the process.

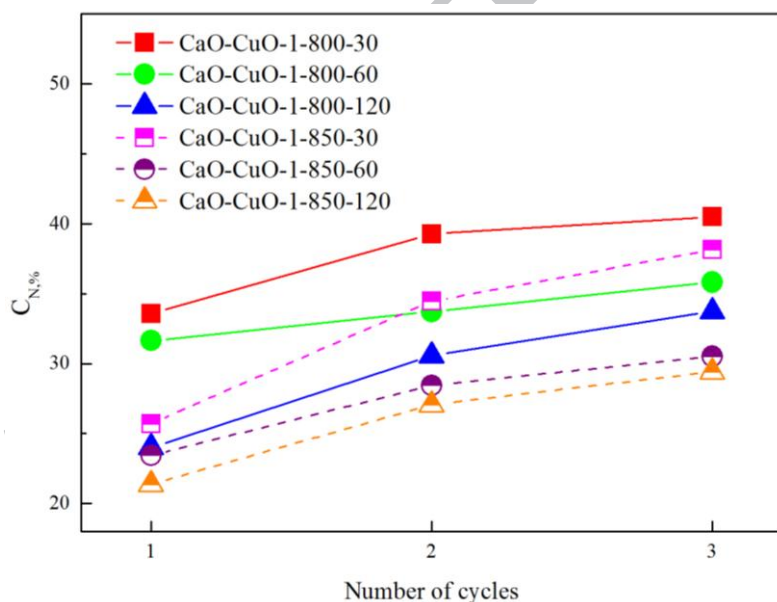


**Fig. 4.** CO<sub>2</sub> uptake capacity of CaO/CuO matrix composites synthesized under different combustion temperatures and durations.

Interestingly, it seems that, compared to their effect on the CO<sub>2</sub> uptake capacity, both combustion temperature and duration had negligible effects on the O<sub>2</sub> carrying capacity of the CaO/CuO matrix composites (Fig. 5). Despite an increase in combustion temperature or duration, there was no obvious change in O<sub>2</sub> carrying capacity of the CaO/CuO matrix composites. All CaO/CuO matrix composites possessed excellent O<sub>2</sub> carrying capacities and the oxidation conversions of all composites were higher than 90%. De Diego et al. [38] demonstrated that the O<sub>2</sub> carrying capacity of pure CuO without any support decreased rapidly with increased cycle number, with an oxidation conversion of only 10% after more than 20 min after only three redox cycles. The excellent and cyclically stable O<sub>2</sub> carrying capacity of CuO in CaO/CuO matrix composites strongly indicates that CaO can function as a support and effectively prevents the decline in reactivity of composites, a finding in line with previous studies [13,14].

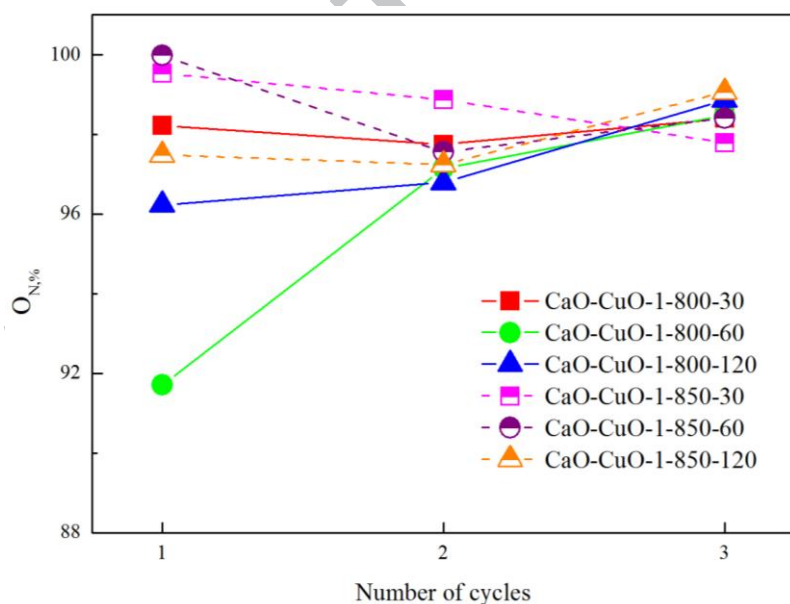


**Fig. 5.** O<sub>2</sub> carrying capacity of CaO/CuO matrix composites synthesized under different combustion temperatures and durations.

CaO/CuO (1:1) matrix composites synthesized at a combustion temperature of 800°C for 30 min exhibited the highest CO<sub>2</sub> uptake capacity and excellent O<sub>2</sub> carrying capacity, with the CO<sub>2</sub> uptake capacity being the keystone of the CaL-CLC process. Additionally, a lower combustion temperature and shorter duration mean lower energy consumption, thus decreasing the preparation cost of the composites. Therefore, a combustion temperature of 800°C and a duration of 30 min were selected for the synthesis of CaO/CuO matrix composites with various molar ratios of CaO to CuO.

### 3.2. Effects of the molar ratio of CaO to CuO

Fig. 6 shows the CO<sub>2</sub> uptake capacity of CaO/CuO matrix composites synthesized with various molar ratios of CaO to CuO in 15 repeated carbonation/calcination and redox cycles. The molar ratio of CaO to CuO present in the CaO/CuO matrix composites exerted a significant influence on the CO<sub>2</sub> uptake capacity of the composites. In terms of the initial CO<sub>2</sub> uptake capacity, CaO-CuO-3-800-30 exhibited the lowest initial carbonation conversion, whereas CaO-CuO-2-800-30 presented the highest initial carbonation conversion, approximately 2.5 times higher than that of CaO-CuO-3-800-30. After 15 cycles, however, CaO-CuO-1-800-30 showed the highest final carbonation conversion while CaO-CuO-3-800-30 exhibited the lowest final conversion.

Furthermore, as shown in Fig. 6, the increase in CO<sub>2</sub> uptake capacities of CaO-CuO-3-800-30 and CaO-CuO-1-800-30 was sustained with increasing cycle numbers. Moreover, the carbonation conversion of CaO-CuO-0.5-800-30 first tended to increase and then decreased,

reaching a maximum carbonation conversion at the seventh cycle. However, it should be noted that the final carbonation conversion of CaO-CuO-0.5-800-30 was still higher than the original value, despite the decay in CO<sub>2</sub> uptake capacity after the seventh cycle. Further, the carbonation conversions of CaO-CuO-2-800-30 did not change significantly with cycle number compared to the other three CaO/CuO matrix composites described above, which fluctuated to some extent over the 15 cycles. Still, the final carbonation conversion was slightly higher than at the beginning. The detailed values of carbonation conversions for various CaO/CuO matrix composites are available in Supplementary Table S4. Therefore, self-activation always occurred during 15 repeated calcination/reduction, oxidation and carbonation cycles for the different molar ratios of CaO to CuO in the CaO/CuO matrix composites.

For the best composite material synthesized, i.e., CaO-CuO-1-800-30, an additional test including 40 repeated cycles was performed in the TGA to examine the stability of self-activation, as shown in Supplementary Fig. S2. It is worth mentioning that from cycle number 15 onwards, the CO<sub>2</sub> uptake capacity of CaO-CuO-1-800-30 was very stable, indicating the effectiveness of self-activation. Moreover, as shown in Supplementary Fig. S3, the successive carbonation curves were quite similar in shape, consisting of a rapid mass growth, commonly termed the kinetically-controlled stage, followed by a transition into a stage with relatively slower mass increase, termed the diffusion-controlled stage. The carbonation conversion of CaO-CuO-1-800-30 with a short carbonation duration of 5 min increased more significantly compared to that with the remaining duration (i.e., 25 min), which accounted for the majority of the CO<sub>2</sub> uptake capacity, as shown in Supplementary Table S5. This result demonstrated that self-activation played an important role in enhancing CO<sub>2</sub> uptake capacity of the kinetically-controlled stage of carbonation and thus allowed the composites to work well for short residence times in a carbonation reactor. It is of significant importance for practical applications of CaL-

CLC process, since  $\text{CO}_2$  capture is limited by short residence time in practical fluidized bed, constraining it to the kinetically-controlled stage [39,40]. To the best of our knowledge, CaO/CuO matrix composites synthesized by SCS are the first to demonstrate self-activation during repeated cycles among the various synthesis approaches adopted, indicating the significant superiority and potential of CaO/CuO matrix composites synthesized by SCS.

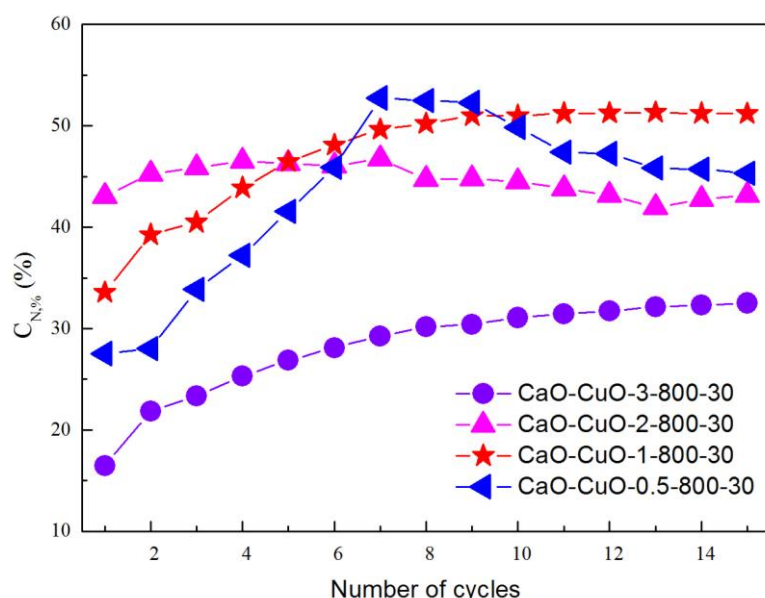


**Fig. 6.**  $\text{CO}_2$  uptake capacity of CaO/CuO matrix composites synthesized with various molar ratios of CaO to CuO.

Fig. 7 illustrates the cyclic  $\text{O}_2$  carrying capacity of  $\text{CuO}^*$  and CaO/CuO matrix composites with various molar ratios of CaO to CuO. Despite the variation in the molar ratio of CaO to CuO in the composites, there was no obvious difference in  $\text{O}_2$  carrying capacity of the four composites. All CaO/CuO matrix composites exhibited excellent and cyclically stable  $\text{O}_2$  carrying capacities. The oxidation conversions of all CaO/CuO matrix composites were always greater than 90%, except for the initial oxidation conversions of CaO-CuO-0.5-800-30 (88.4%) and CaO-CuO-2-800-30 (88.7%). These results strongly indicate that the CaO/CuO matrix

composites synthesized by SCS possessed excellent and cyclically stable  $O_2$  carrying capacities. The redox reactivity of CaO/CuO matrix composites was so high that with our equipment it appeared as a single reaction step (Supplementary Fig. S2).

In addition, as shown in Fig. 7, the  $O_2$  carrying capacity of CuO\* decreased significantly, and reached an extremely low oxidation conversion of 18.1% after only five cycles. The rapid decline in  $O_2$  carrying capacity of CuO\* with increasing cycle number is in agreement with previous studies [38,41,42], which have ascribed the deactivation mainly to the thermal sintering of Cu/CuO. This result further validates the support effect of CaO on CuO in the CaO/CuO matrix composites.

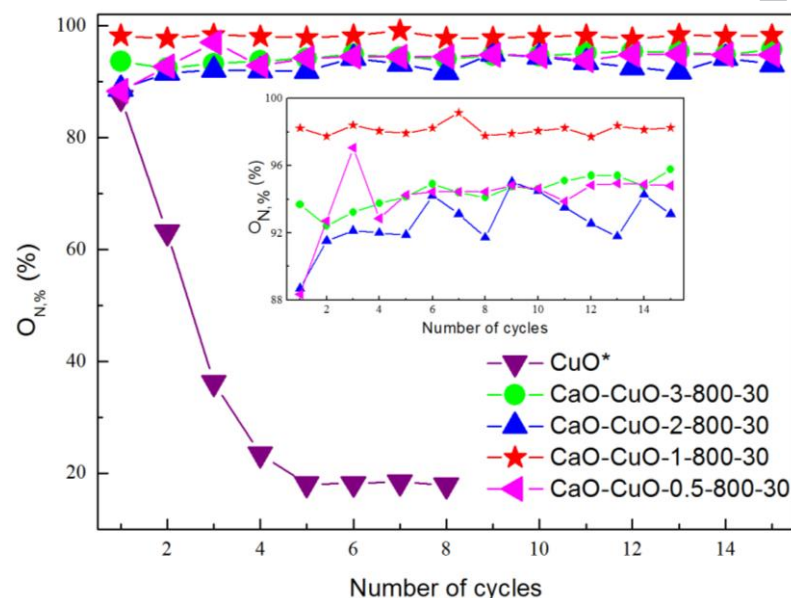


**Fig. 7.**  $O_2$  carrying capacity of CaO/CuO matrix composites synthesized with various molar ratios of CaO to CuO, and CuO\*.

### 3.3. Microstructure analysis

The sorption capacity of a sorbent is generally considered to be related to its specific surface area and pore volume. The specific surface area of CaO-CuO-1-800-30 increased from  $30.7 \text{ m}^2\cdot\text{g}^{-1}$  to  $37.4 \text{ m}^2\cdot\text{g}^{-1}$  over the 15 repeated cycles, while the corresponding pore volume increased from  $0.0475 \text{ cm}^3\cdot\text{g}^{-1}$  to  $0.0551 \text{ cm}^3\cdot\text{g}^{-1}$ . As shown in Fig. 8, there is a clear increase in the pore size distribution of 2-50 nm when CaO-CuO-1-800-30 underwent 15 repeated cycles, which is beneficial for  $\text{CO}_2$  uptake capacity since it plays a critical role in  $\text{CO}_2$  capture [26]. The increases of both specific surface area and pore volume lead to the increase of  $\text{CO}_2$  uptake capacity, i.e., the occurrence of self-activation. Therefore, the self-activation phenomenon observed in this work can be explained by a pore-skeleton model, which has been widely accepted by many researchers [32-37]. A hard and stable skeleton was formed during the repeated calcination/reduction, oxidation and carbonation cycles, thus enhancing the solid-state diffusion carbonation in the first cycle. A quick calcination/reduction and oxidation following an enhanced diffusive carbonation stage leads to a renovated porous skeleton with increased surface area and pore volume for the next carbonation, subsequently leading to an increase in  $\text{CO}_2$  uptake capacity.

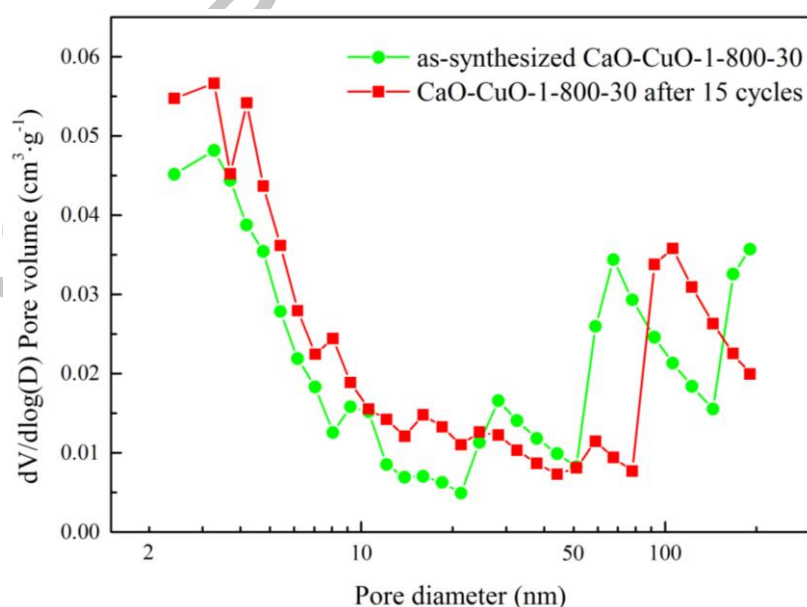


**Fig. 8.** Pore size distributions of CaO-CuO-1-800-30 before and after 15 repeated cycles.

The particle size distributions of the as-synthesized CaO/CuO matrix composites and CuO\* are shown in Supplementary Fig. S4. It was found that both CuO\* and the CaO/CuO matrix composites presented a relatively narrow particle size distribution, and a decrease in the molar ratio of CaO to CuO led to an increase in particle size. The SEM-EDX mappings of the surfaces of the as-synthesized CaO/CuO matrix composites are shown Supplementary Fig. S5. Ca and Cu elements were dispersed homogeneously on the surface of the composites, revealing that SCS yielded a fairly homogeneous distribution of CaO and CuO in the CaO/CuO matrix composites. This ensured excellent heat and mass transfer between the redox cycle and the carbonation/calcination cycle, which is an essential factor for CaL-CLC process.

Fig. 9 shows the TEM images of the as-synthesized CaO/CuO matrix composites and CuO\*, respectively. The CaO/CuO matrix composites synthesized by SCS were nanostructured with grain sizes below 200 nm, which is highly advantageous since this reduces the diffusion path lengths of CO<sub>2</sub> in the sorbent, leading in turn to high rates of CO<sub>2</sub> uptake [31]. This is mainly due to the formation of various gases during SCS process, which inhibits particle size growth and favours synthesis of nano-structure materials with high specific surface area [24,25]. It is interesting to notice that large amounts of mesopores were found in the interiors of grains, as shown in Fig. 9d, which was considered to be beneficial for CO<sub>2</sub> uptake [26,27]. Moreover, the shape of the grains in the CaO/CuO matrix composites differed greatly with a decreasing molar ratio of CaO to CuO in the composites, changing from nearly spherical to long strips.

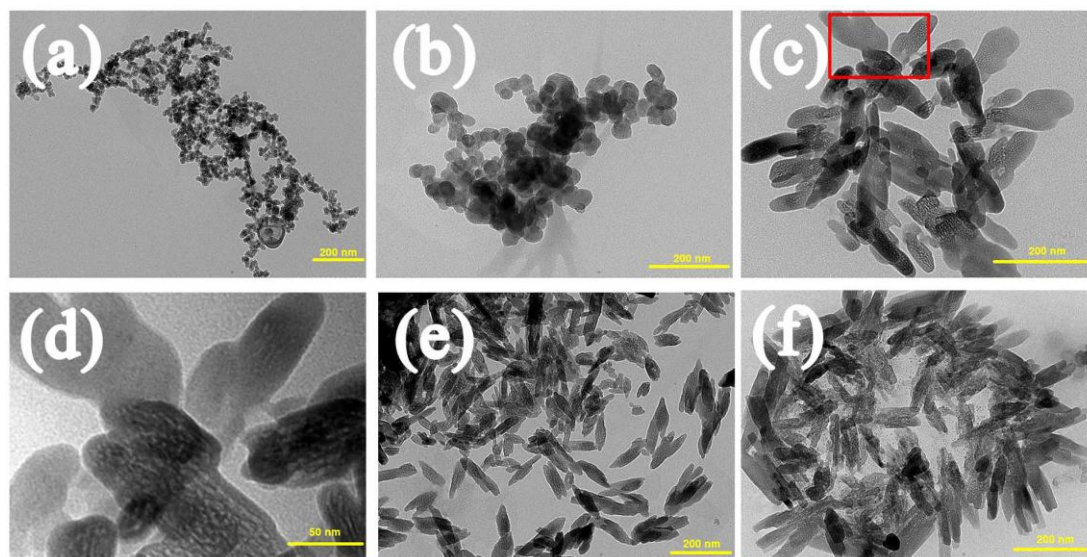


**Fig. 9.** TEM images of the as-synthesized CaO/CuO matrix composites and CuO\*. (a): CaO-CuO-3-800-30 (b): CaO-CuO-2-800-30; (c): CaO-CuO-1-800-30; (d): CaO-CuO-1-800-30 in high magnification (marked area in (c)); (e): CaO-CuO-0.5-800-30; (f): CuO\*.

The surface morphology of the CaO/CuO matrix composites and CuO\* varied substantially when comparing SEM images of the samples taken before and after the TGA tests, as shown in Supplementary Figs. S6, S7. The original CaO/CuO matrix composites possessed a low porosity; however, more porous and irregular surfaces were obtained after 15 cycles. Moreover, the grains present in the surface of the composites became smaller than those in the as-synthesized material, which may have partially contributed to the phenomenon of self-activation observed in Fig. 6. As mentioned above, the carbonation reaction consists of two stages: an initially fast, kinetically-controlled stage, followed by a substantially slower, diffusion-controlled stage. The transition between the fast and slow reaction stages takes place in a critical carbonation conversion when the thickness of the  $\text{CaCO}_3$  product layer reaches about 50 nm [43]. Thus, by the shrinkage of the size of grains, the  $\text{CO}_2$  uptake capacity in the kinetically-controlled stage can be improved, as shown in Supplementary Table S5 and Fig. S3 [44,45].

Furthermore, it was clearly observed that significant differences existed in the surface morphology of CuO\* when CuO\* underwent eight repeated redox cycles. The previous porous appearance of CuO\* disappeared and a smooth and compact surface with low porosity formed; however, the several cracks observed after eight cycles confirmed the severe sintering of CuO/Cu over repeated redox cycles. This is consistent with the TGA results (Fig. 7), wherein the oxidation conversion of CuO\* declined rapidly as the cycle number increased.

### 3.4. XRD analysis

The main crystalline phases in all as-synthesized CaO/CuO matrix composites were CaO, CuO and  $\text{Ca}_2\text{CuO}_3$ , as identified by ex-situ XRD (Supplementary Fig. S8). The progress of the carbonation/calcination and redox reactions, together with the corresponding change of phases, was tracked over three reaction cycles by in-situ XRD. During the initial heating stage from room temperature to 650°C, there was no change in the compositions of the four CaO/CuO matrix composites (Supplementary Fig. S9). However, after the first calcination/reduction stage at 800°C, the  $\text{Ca}_2\text{CuO}_3$  phase disappeared and was not detected again during the following reaction stages, as shown in Fig. 10 and Supplementary Figs. S10-S12. It can be inferred that the presence of  $\text{Ca}_2\text{CuO}_3$  can be related to the oxidizing atmosphere and/or the high temperature (over 800°C) in the preparation procedure. Besides, it confirmed that  $\text{Ca}_2\text{CuO}_3$  is an active phase, which decomposed into CaO and Cu during the calcination/reduction stage. Similar observation was made by Kierzkowska and Müller, who showed that calcium present in the form of  $\text{Ca}_2\text{CuO}_3$  was active for  $\text{CO}_2$  capture [15]. Meanwhile, Cu was present because of the reduction reaction between CuO and  $\text{CH}_4$ . After the subsequent oxidation reaction, all of the Cu was oxidized to CuO, and  $\text{Cu}_2\text{O}$  was not detected in the composites, indicating the good redox reactivity of CaO/CuO matrix composites. Finally,  $\text{CaCO}_3$  was detected via the carbonation of CaO.

However, CaO still existed after the carbonation stage, which suggests the incomplete reaction between CaO and CO<sub>2</sub>, in agreement with the results from the TGA (Fig. 6). All of these results confirmed that no side reactions had taken place between CaO/CaCO<sub>3</sub> and CuO/Cu in this process, making CaO/CuO matrix composites an attractive candidate for the CaL-CLC process. Additionally, there was no significant difference between the three cycles for each CaO/CuO matrix composite, and the phase composition for each composite remained the same.

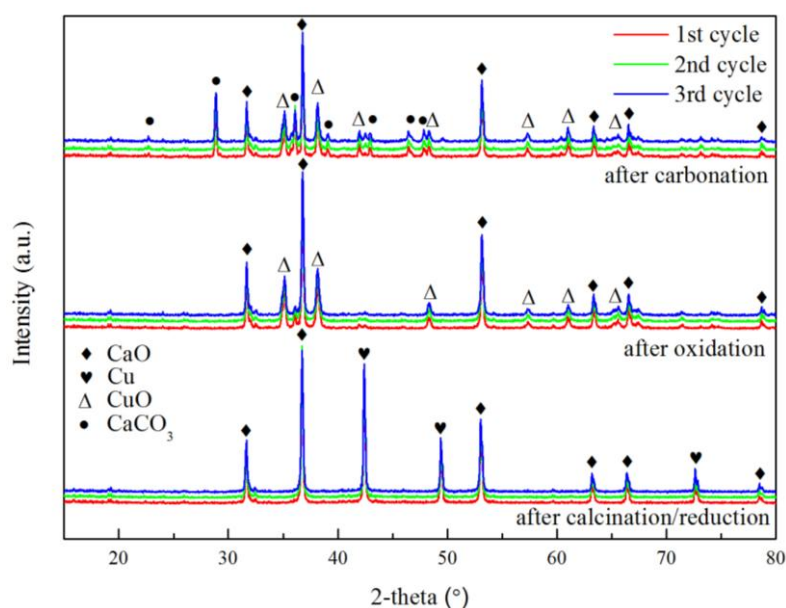


**Fig. 10.** In-situ XRD diffractograms of CaO-CuO-3-800-30 during three repeated calcination/reduction, oxidation and carbonation cycles.

Figs. 11, 12 and Supplementary Figs. S13, S14 show the in-situ XRD diffractograms for the four CaO/CuO matrix composites recorded during the oxidation stage. When the molar ratio of CaO to CuO was 2 or 3, Cu was fully oxidized to CuO after the second measurement, i.e., after 150 s. For the remainder of the oxidation period (after the second measurement), the phase compositions of the CaO/CuO matrix composites did not vary significantly and the only phases detected were CaO and CuO (Fig. 11 and Supplementary Fig. S13). However, when the molar

ratio of CaO to CuO was 0.5 or 1, the oxidation of Cu was somewhat slower and proceeded via  $\text{Cu}_2\text{O}$  as an intermediate, as shown in Fig. 12 and Supplementary Fig. S14. After the second measurement, only  $\text{Cu}_2\text{O}$ , Cu and CaO were detected. With the progress of the oxidation reaction, Cu disappeared and was oxidized to  $\text{Cu}_2\text{O}$  while only part of the  $\text{Cu}_2\text{O}$  was further oxidized to CuO until the fifth measurement. After the tenth cycle, all remaining  $\text{Cu}_2\text{O}$  was fully converted to CuO, and CaO and CuO were the only two phases detected. This result can be attributed to the stoichiometric ratio of Cu to  $\text{O}_2$ . When the ratio is large, Cu is first oxidized to  $\text{Cu}_2\text{O}$  (Eq. (7)), followed by further oxidation of  $\text{Cu}_2\text{O}$  to CuO (Eq. (8)). With the decrease of the stoichiometric ratio of Cu to  $\text{O}_2$ , the reaction rate of Eqs. (7), (8) increased significantly. Once the  $\text{Cu}_2\text{O}$  phase was formed, it was oxidized to CuO immediately.

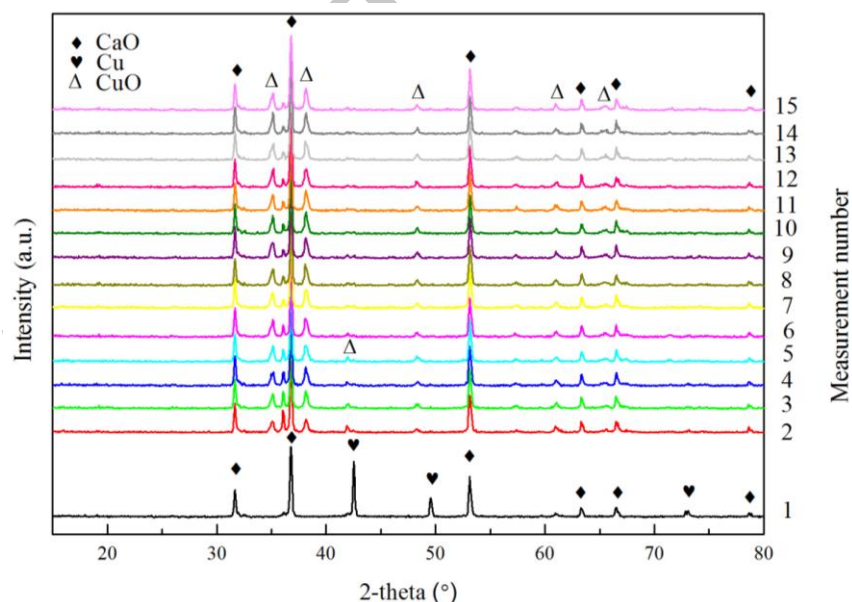


**Fig. 11.** In-situ XRD diffractograms for CaO-CuO-3-800-30 during the oxidation stage.

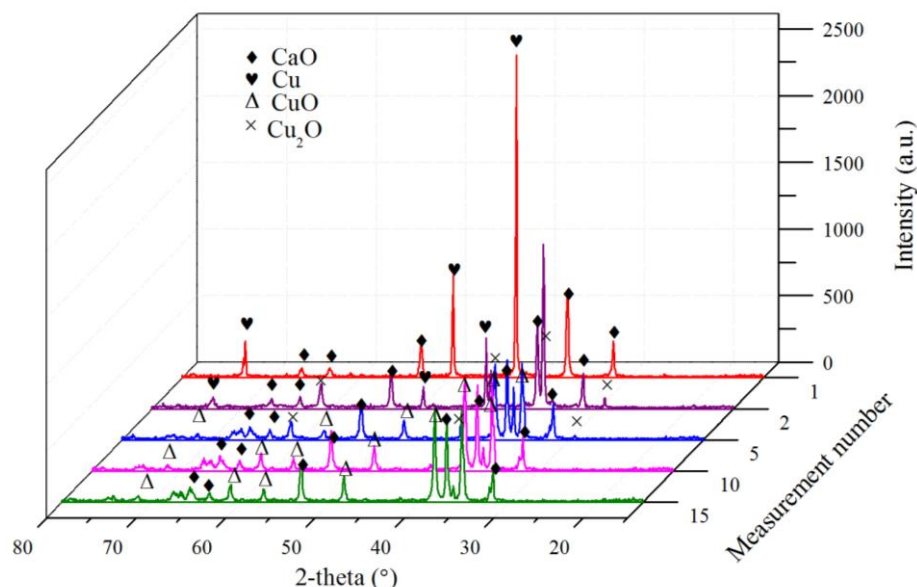


**Fig. 12.** In-situ XRD diffractograms for CaO-CuO-1-800-30 during the oxidation stage.

The in-situ XRD diffractograms for the four CaO/CuO matrix composites during the carbonation stage are shown in Fig. 13 and Supplementary Figs. S15-S17.  $\text{CaCO}_3$  was detected after the second measurement, and only CaO,  $\text{CaCO}_3$  and CuO were detected during the carbonation reaction. The result revealed that only the carbonation of CaO took place and no side reactions occurred between CaO/ $\text{CaCO}_3$  and CuO during this stage. Furthermore, it is confirmed that CuO was not decomposed into Cu or  $\text{Cu}_2\text{O}$  during the carbonation stage, which is of significant practical value. The premature release of  $\text{O}_2$  derived from CuO in the carbonation reactor instead of the calcination/reduction reactor, could lead to less  $\text{O}_2$  to react with  $\text{CH}_4$  and thus provide insufficient heat for the calcination of  $\text{CaCO}_3$ . As a result, the  $\text{CO}_2$  capture performance of CaO/CuO matrix composites would decrease.

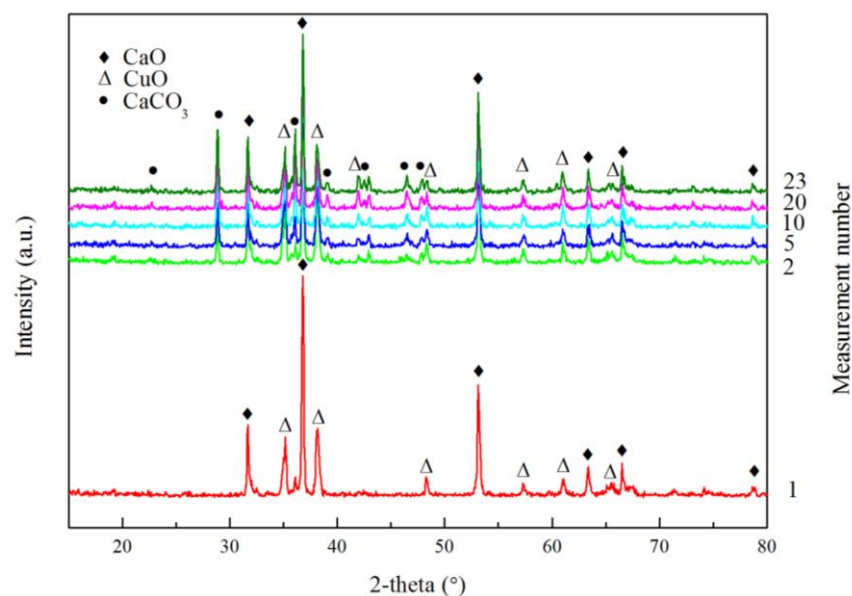


**Fig. 13.** In-situ XRD diffractograms for CaO-CuO-3-800-30 during the carbonation stage.

#### 4. Conclusions

In this work, a simple but effective approach, SCS, was first used to synthesize various nanostructured CaO/CuO matrix composites with homogenous elemental distributions. This feature was confirmed by TEM and SEM-EDX. The cyclic CO<sub>2</sub> uptake capacity and redox characteristics of CaO/CuO matrix composites were evaluated. To date, self-activation, i.e., an increase of CO<sub>2</sub> uptake capacity with repeated cycles, was first observed in this work, in contrast to the rapid decay in CO<sub>2</sub> uptake capacity typically reported in previous work. Moreover, self-activation could significantly enhance the CO<sub>2</sub> uptake capacity of CaO/CuO matrix composites during the kinetically-controlled stage of carbonation, which is of significant value for practical application of CaL-CLC technology. The self-activation can be mainly attributed to the increase of both specific surface area and pore volume. The O<sub>2</sub> carrying capacity of CaO/CuO matrix composites was excellent and cyclically stable as a result of the support effect of CaO. In addition, the effects of the synthesis parameters (combustion temperature and duration) and the

molar ratio of CaO to CuO in the composite on the performance of composites were analyzed. It was found that an increase in both combustion temperature and duration resulted in a relatively clear decrease in CO<sub>2</sub> uptake capacity of the CaO/CuO matrix composites compared to their O<sub>2</sub> carrying capacity. Variation of the molar ratio of CaO to CuO led to the significant changes in CO<sub>2</sub> uptake capacity, but exerted negligible effects on O<sub>2</sub> carrying capacity. Among the CaO/CuO matrix composites, CaO-CuO-1-800-30 possessed the best CO<sub>2</sub> uptake and O<sub>2</sub> carrying capacity after 15 repeated cycles, i.e., 51.2% and 98.3%, respectively. On the basis of the in-situ XRD results, it can be concluded that no side reactions occurred between CaO/CaCO<sub>3</sub> and CuO/Cu in this process, and that the phase Ca<sub>2</sub>CuO<sub>3</sub> formed in the preparation procedure was an active component for CO<sub>2</sub> capture. All of these results make this novel composite material a promising candidate for CaL-CLC process.

## Notes

The authors declare no competing financial interest.

## Acknowledgements

The authors wish to acknowledge the financial support from the National Natural Science Foundation of China through Grant No. 51776039, the Fundamental Research Funds for the Central Universities, and the Swiss National Science Foundation through Grant No. 200020\_156015).

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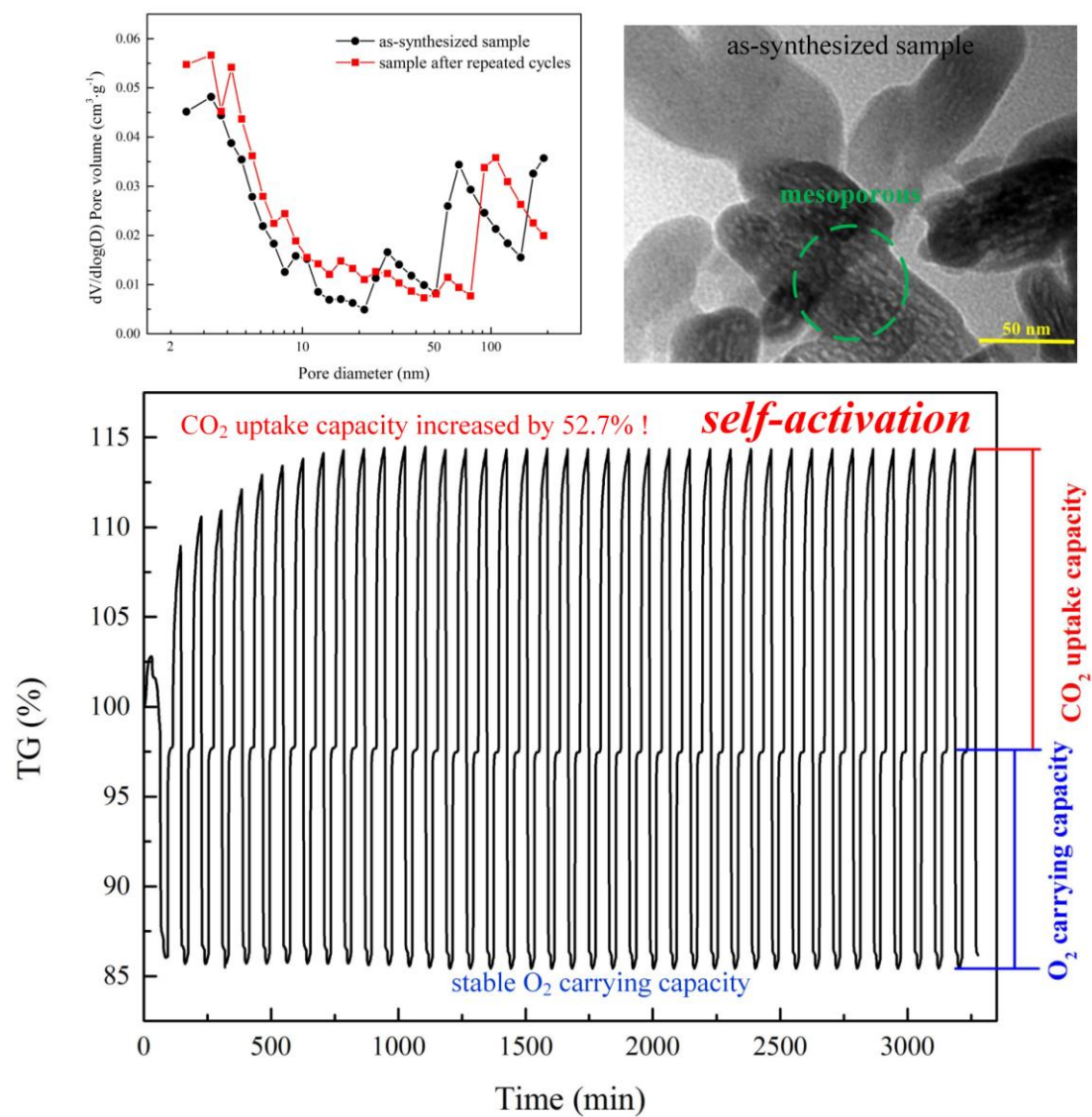
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ACCEPTED MANUSCRIPT

## Graphical abstract



### Highlights

- SCS was first used to synthesize nanostructured CaO/CuO matrix composites.
- Self-activation phenomenon was first reported in CaL-CLC process.
- No side reactions occurred between CaO/CaCO<sub>3</sub> and Cu/CuO during the process.



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## **Self-activated, Nanostructured Composite for Improved CaL-CLC technology**

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**2018-06-28**

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<https://doi.org/10.1016/j.cej.2018.06.176>

Jian Chen, Lunbo Duan, Felix Donat, et al., Self-activated, Nanostructured Composite for Improved CaL-CLC technology. Chemical Engineering Journal, Volume 351, Issue November, 2018, pp. 1038-1046