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Behavior of CaO/CuO Based Composite in a Combined Calcium and Copper Chemical Looping Process

Changlei Qin,[†] Junjun Yin,[†] Wenqiang Liu,[‡] Hui An,[§] and Bo Feng^{*,†}

[†]School of Mechanical and Mining Engineering, The University of Queensland, St Lucia, Queensland 4072, Australia

[‡]State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

[§]School of Chemical Engineering, The University of Queensland, St Lucia, Queensland 4072, Australia

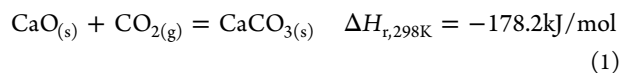
Supporting Information

ABSTRACT: Integration of chemical looping combustion into calcium looping is an attractive approach to solving the problem of energy requirement for the regeneration of CaO-based sorbent. In this work, the behavior of MgO supported CaO/CuO composite in the new combined process (CaCuCL) was investigated. The composite was prepared via a simple wet mixing method and measured via a thermogravimetric analyzer for its chemical performance. It appears that the component of Cu/CuO has a significant influence on the cyclic performance of CaO, which is probably caused by the “wrapping” of Cu/CuO outside, due to its low melting point. However, this negative effect can be greatly reduced by using appropriate operating conditions in the successive reactions. When tested for 68 cycles, all synthetic sorbents showed good reactivity and stability of the Cu/CuO component, although loss-in-capacity of CaO was still observed.

1. INTRODUCTION

The use of low-carbon or carbon-free alternative energy and increasing the efficiency of fuel utilization are the most important strategies to solve the problem of global warming, which was mainly caused by anthropogenic CO₂ emissions from fossil fuel combustion.^{1,2} Unfortunately, limited by technical and economic factors, these routes cannot be effectively implemented in a short time. In recent years, considerable attention has been placed on CO₂ capture and sequestration (CCS), which as a strategy is believed to be able to contribute to 15–55% of the cumulative mitigation of atmospheric CO₂ by 2100.³

CCS mainly involves three steps, first to collect and concentrate CO₂ from emission sources like large fossil fuel power plants, transport it to a suitable storage location by pipeline system or ships, and then store it away from the atmosphere for a long period of time.³ Among these steps, CO₂ capture is the major barrier due to issues relating to the technical feasibility and cost.⁴ Thus, there is great interest worldwide in the development of CO₂ capture technologies and among which, the calcium looping cycle (CaL) is particularly interesting for its abundant cheap sorbent precursors and the potential high CO₂ carrying capacity in both post-^{5,6} and precombustion^{7–11} CO₂ capture.



The calcium looping cycle is based on the reversible chemical reactions between CaO and CO₂, as shown in reaction 1. When the forward reaction (carbonation) occurs, CO₂ is captured to produce calcium carbonate in the carbonator. Then, calcium oxide is regenerated in the calciner through the backward reaction (calcination) and recycled back ready for the next

cycle. During calcination, pure CO₂ stream is released from the sorbent and the objective of gas separation is achieved.

In recent years, good progress has been made in the development of calcium looping technology, for example, several pilot plant trials have been initiated at INCAR-CSIC (Spain),¹² University of Stuttgart (Germany),¹³ Canmet-ENERGY (Canada),¹⁴ Ohio State University (USA),¹⁵ and Vienna University of Technology (Austria),¹⁶ etc.

Despite a number of distinctive advantages, CaL technology faces one problem that extra energy is always required for the decomposition of CaCO₃, which is inherently endothermic. Currently, in order to produce CO₂-rich stream suitable for subsequent compression and geological storage, oxygen combustion of fuel has been proposed to be applied in the calciner. However, an air separation unit is needed for oxygen production which is energy intensive and costly, and could largely affect the economics of the CaL process. The CaL process would be more economically competitive if the air separation unit can be eliminated.

One possible method to remove the expensive air separation unit from calcium looping cycle is using chemical looping combustion (CLC) to supply energy for the regeneration of calcium oxide. The novel concept was based on the idea of energy supply for reaction by CLC process first proposed by Lyon et al.¹⁷ and then developed for steam reforming,¹⁸ where Ni/NiO was chosen as the oxygen carrier in CLC. By coupling the exothermic reaction of Ni oxidation and the endothermic decomposition of calcium carbonate together, a higher efficiency and lower cost can be achieved, since the heat is

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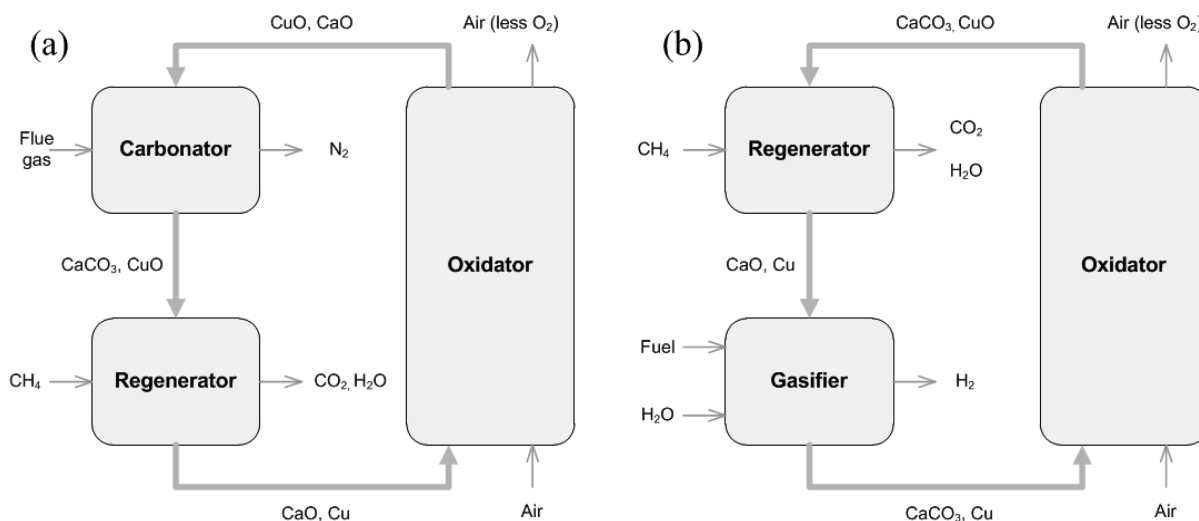
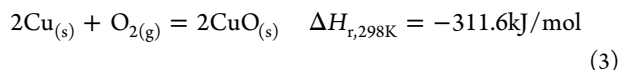
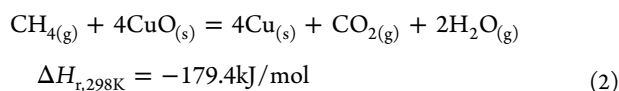


Figure 1. Schematics of combined calcium and copper chemical looping for (a) postcombustion and (b) precombustion.

transferred directly from the metal to the carbonate. However, the problem of CO₂ emission to atmosphere was left unsolved in this process. Later, Abanades et al.^{19,20} and Feng²¹ independently proposed integrating chemical looping combustion using Cu/CuO oxygen carrier with calcium looping. In this method, the energy needed for calcination of CaCO₃ can be supplied by exothermic reduction of CuO with fuel gases like CH₄ (reaction 2), CO and H₂, without producing difficult-to-separate gases in the product gas stream. The other two reactions: carbonation of CaO and oxidation of Cu (reaction 3) are both exothermic and the energy can be recovered for steam generation. Figure 1 shows the schematic diagrams of its application in postcombustion and precombustion CO₂ capture systems, for the latter process, a preliminary design has been completed and a good potential for high efficiency was recently reported.²²



Recently, some experimental work on the application of CaO/CuO composite in CaCuCL was published by Anthony et al.^{23–25} Several kinds of core-in-shell pellets were synthesized using limestone, CuO and calcium aluminate cement via a mechanical pelletizer, and their chemical and mechanical properties were tested in a TGA and a bubbling fluidized bed, respectively. It shows that the reactivity of Cu/CuO can be sustained, however, loss-in-capacity of CaO was found even in short calcination/reduction, oxidation, and carbonation cycles. Attrition seems not to be a problem for the pellets as no obvious mass loss was observed both at room and at temperature of 800 °C. Furthermore, several possible schemes of the concept were discussed. Kierzkoska et al.²⁶ developed calcium-based, copper-functionalized CO₂ sorbents with a coprecipitation technique and tested their performances.

Although the concept of combined calcium and copper chemical looping demonstrates some attractive advantages in potential applications, few works have been done to study the behavior of the CaO/CuO based composite in the successive reactions of calcination/reduction, oxidation, and carbonation.

The main objective of this report is to explore the potential technical problems in the CaCuCL process, to determine the optimum operating conditions and to identify suitable CaO/CuO composites under these conditions for postcombustion CO₂ capture.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Composite. In this work, a composite CaO-CuO-MgO sorbent was synthesized with a CaO/CuO molar ratio of 0.25. This value was determined based on energies of reactions 1 and 2, assuming that an energy balance can be achieved in the regenerator between the exothermic reduction of CuO with CH₄ and the endothermic decarbonation of CaCO₃. It should be noted that the ratio of CaO/CuO in the composite will change if other fuel gas, such as CO, H₂ and syngas, was employed as reducing agent. Additionally, MgO was adopted in the composite as inert support to maintain the reactivity of CaO and CuO during cyclic reactions. Thus, the mass fraction of CaO, CuO, and MgO in the final composite (at oxidized state) was 11.24%, 63.76%, and 25%, respectively.

The fresh CaO-CuO-MgO was prepared through a wet mixing method^{27,28} with calcium acetate and copper(II) acetate as active phase precursors, and magnesium acetate as support precursor. The objective is to obtain CaO/CuO based composite uniformly dispersed on MgO support, giving sufficiently high reactivity during successive cycles of calcination/reduction, oxidation, and carbonation. First, predetermined amounts of calcium acetate hydrate (99.0–100.5%, Sigma-Aldrich), copper(II) acetate (98.0–102.0%, Ajax Finechem) and magnesium acetate (99.5–102.0%, Ajax Finechem) were separately dissolved in distilled water with heat treatment to promote this process. The three solutions were then mixed in sequence and dried overnight at 110 °C, which was subsequently precalcined in air for 1.5 h.

2.2. Characterization of the Composite. Phase composition of the samples was analyzed in a Bruker AXS D8 Advance X-ray diffractometer equipped with a scintillation counter, graphite monochromator and copper target over the angular range 10–80° (2θ) in 0.02° Step Size and 20 s per step at 40 kV, 30 mA and 20 mm variable slits. Traces were processed using the Diffrac^{plus} Evaluation Package Release 2009 and PDF-2 2009.

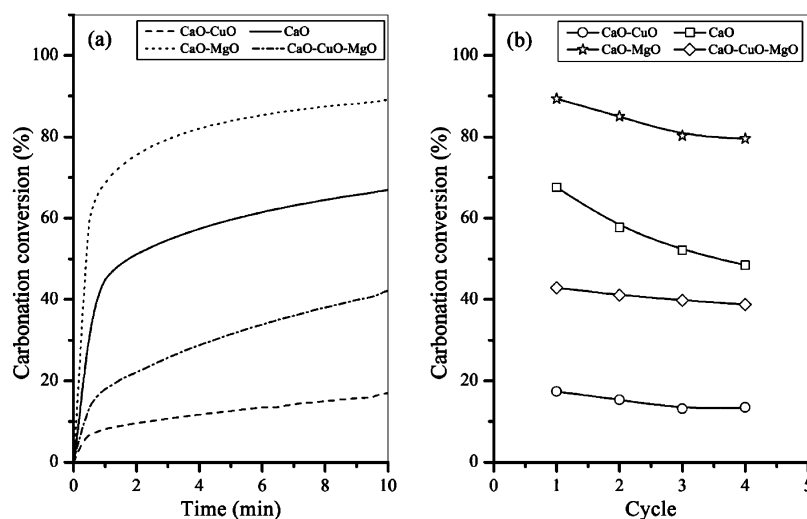


Figure 2. (a) Carbonation curves in the 1st cycle, and (b) cyclic carbonation conversions of samples with different components. All samples were precalcined at 900 °C for 1.5 h, then tested in the following condition: calcination/reduction in 15% CH₄ at 800 °C for 10 min, oxidation in air and carbonation in 15% CO₂, both at 650 °C for 10 min.

A JEOL JSM-6610 Scanning Electron Microscope (SEM) was used to investigate morphologies of selected composites. Before image capturing, the sample powders were dispersed on a conductive adhesive carbon tab placed on an SEM mount and coated with platinum using EIKO IB-5 Sputter Coater for 3 min (approximately 10 nm thick) to obtain better electronic signal. All SEM images were obtained from secondary electrons with 20 kV of accelerating voltage.

The specific BET surface area and pore volume of selected composites were determined with the N₂ adsorption/desorption isotherms obtained at approximately −196 °C using a Micromeritics TriStar 3000 instrument after outgassing under vacuum for 18 h at 200 °C.

2.3. Reactivity Tests. The testing of chemical performance was carried out in a Cahn thermogravimetric analyzer (TGA, model 121). Around 40 mg composite was placed on a quartz pan, which was suspended in a quartz tube and then exposed to alternating calcination/reduction, oxidation and carbonation conditions. It should be noted that preliminary tests showed that the results were not affected by sample size under the testing conditions as shown in Supporting Information. Typically, the experiment was initiated by heating TGA to 800 °C at a rate of 20 °C/min in 85 mL/min of nitrogen, then calcination/reduction was conducted at this temperature for 10 min under a flow containing 15 mL/min CH₄ and 85 mL/min N₂. After this process, the flow of CH₄ was stopped and TGA was cooled to 650 °C at a rate of −20 °C/min. Then, Cu was oxidized back to CuO in air (85 mL/min) for 10 min, and carbonation followed in a flow of 15 mL/min CO₂ and 85 mL/min N₂ for 10 min at the same temperature. Furthermore, set points of calcination/reduction temperature and oxidation/carbonation temperature would vary in 800–950 °C and 600–800 °C, respectively, when their effects on the reactivity of composite were investigated. During TGA test, data of sample mass were monitored and conversions of Cu and CaO were calculated on the basis of mass change, assuming mass change was only caused by the formation and decomposition of calcium carbonate and reduction/oxidation of CuO/Cu.

2.4. Data Analysis. The reactivity of CaO and Cu in the composite is separately quantified in the terms of conversion (X_{car} and X_{oxi}), and is defined as the fraction of CaO carbonated

or Cu oxidized. The carbonation conversion of CaO and the oxidation conversion of Cu were calculated as follows:

$$X_{\text{car}} = \frac{(m_1 - m_0) \cdot M_{\text{CaO}}}{m_0 \cdot \varphi_{\text{CaO}} \cdot M_{\text{CO}_2}} \cdot 100\%$$

$$X_{\text{oxi}} = \frac{(m_2 - m_1) \cdot M_{\text{Cu}}}{m_0 \cdot \varphi_{\text{Cu}} \cdot M_{\text{O}}} \cdot 100\%$$

where X_{car} and X_{oxi} are the carbonation conversion of calcium oxide and oxidation conversion of Cu, respectively. m_0 is the mass of composite after calcination/reduction (the composite only contains CaO, Cu and support material at this state). m_1 and m_2 are the masses of the composite in oxidized and carbonated state, respectively. φ_{CaO} and φ_{Cu} are mass fraction of CaO and Cu in the composite after calcination/reduction. M_{CaO} , M_{CO_2} , M_{Cu} and M_{O} are molar mass of CaO, CO₂, Cu, and O, respectively.

3. RESULTS AND DISCUSSION

3.1. Property of the Composite in CaCuCL. The phase composition of sample CaO-CuO-MgO after first reduction, oxidation and carbonation, respectively was obtained (Figure S1 of the Supporting Information, SI). Only CaO and Cu were found in addition to the inert support MgO after calcination/reduction, suggesting that both decomposition of CaCO₃ and reduction of CuO were fully achieved. Moreover, Cu was completely oxidized during oxidation stage, but carbonation of CaO only occurred partially.

The typical mass curve of CaO-CuO-MgO in the successive calcinations/reduction, oxidation and carbonation was also obtained (Figure S2 of the SI). Apparently, weight of the composite after every reduction is constant, indicating that no carbon deposition occurred under the conditions studied.^{26,29} Among the main reactions, the reduction of CuO with CH₄ completes quickly, with a total reaction time of less than 1 min. In contrast, the oxidation of Cu is composed of two steps, an initial stage characterized with a high reaction rate and followed by a sharp decrease in reactivity, though the second stage was not as distinguishable as the diffusion-controlled stage in the carbonation of CaO. These steps should be associated with

different resistances to the global reaction, that is, the chemical reaction and the product layer diffusion, respectively.³⁰ As for the reactivity of CaO and Cu in the successive reactions, only around 43% of CaO in the composite was converted to CaCO₃, while the oxidation conversion of Cu was almost 100%. Therefore, the slowest reaction is the carbonation of CaO, and more attention was paid to this reaction in subsequent studies.

3.2. Loss-in-Capacity Caused by Addition of Cu/CuO.

As discussed previously, the reactivity of CaO in the synthetic CaO-CuO-MgO composite was observed to be very low under mild testing condition. In order to study the reason for this low conversion, three reference samples: CaO, CaO-CuO, and CaO-MgO were prepared using wet mixing method and tested for comparison of the CO₂ sorption performance, and the results were shown in Figure 2. In CaO-CuO, the molar ratio of CaO/CuO is also 0.25 while in CaO-MgO, the mass ratio of CaO/MgO is 0.4496, the same as in CaO-CuO-MgO. For pure CaO, in the first cycle, it shows a carbonation conversion of 67.6% when carbonated in 15% CO₂ at 650 °C for 10 min. The conversion then gradually decreased during subsequent cycles, reaching 48.5% after 4 cycles. Interestingly, the carbonation conversion of CaO-CuO in the first cycle is remarkably lower than pure CaO, only around 17.4% and 13.4% after the fourth cycle. It seems the addition of CuO has a negative effect on the reactivity of the CaO component in the sample. To the contrary, the addition of inert MgO can greatly enhance the chemical performance of CaO, which can be observed from the highest carbonation conversion of 89.3% in the first cycle and a conversion of 79.6% in the fourth cycle. Under the combined negative effect of Cu/CuO and the positive effect of MgO, the synthetic CaO-CuO-MgO demonstrated a carbonation value between that of CaO-CuO and CaO-MgO: 43% initially to 39% at the fourth cycle.

The reference sample of CaO-MgO and composite CaO-CuO-MgO were further tested to investigate the influence of Cu/CuO on CO₂ uptake. They were both precalcined in advance at various temperatures in the range of 400 to 900 °C, then subjected to TGA under the following conditions: calcined/reduced in 15% CH₄ at 800 °C, oxidized in air and carbonated in 15% CO₂ at 650 °C. Figure 3 summarizes the results of the carbonation curves of CaO-CuO-MgO and CaO-MgO. Obviously, the extent of negative effect caused by the addition of Cu/CuO on the reactivity of CaO varies with changing precalcination temperature. The uptake of CO₂ in CaO-MgO was not greatly affected by the precalcination temperature, with the highest value of 93.7% when precalcined at 400 °C and lowest of 89.3% at 900 °C. However, only a carbonation conversion of 76.5% was left when Cu/CuO was introduced into the mixture and precalcined at 400 °C. The decrease of CaO reactivity was severe at the precalcination temperature of 900 °C, 46% lower than that of CaO-MgO.

This decay of carbonation conversion should not be caused by chemical interactions between CaO and CuO or MgO, because only crystals of CaO, CuO, MgO and CaCO₃ or Cu₂O were found from XRD patterns of the composites after calcined at different temperatures, as shown in Figure 4. Some Cu₂O was found after calcination at 900 °C, because CuO becomes unstable and starts to decompose at around 870 °C.^{31–33} To obtain a better understanding of the negative influence of Cu/CuO on the reactivity of CaO, pore surface area, pore volume, and morphology of the 400 and 900 °C precalcined CaO-CuO-MgO after oxidation were investigated by N₂ physisorption and SEM, respectively. The BET surface area of the composite

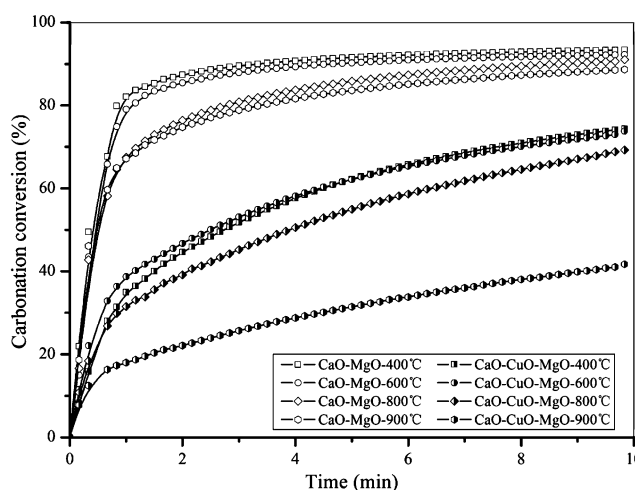


Figure 3. Carbonation conversions of CaO-MgO and CaO-CuO-MgO, which were both precalcined at various temperatures. Testing conditions: calcination/reduction in 15% CH₄ at 800 °C for 10 min, oxidation in air and carbonation in 15% CO₂, both at 650 °C for 10 min.

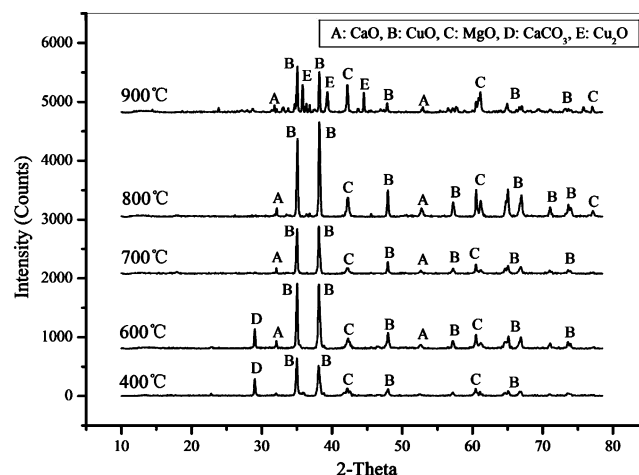


Figure 4. X-ray diffraction patterns of CaO-CuO-MgO after 1.5 h precalcination at the temperature of 400–900 °C.

precalcined at 400 °C is 4.7268 m²/g, which is higher than that of the composite after precalcination at 900 °C (1.7568 m²/g). The BJH adsorption cumulative pore volume was also found to decrease with increasing precalcination temperature, from 0.030261 cm³/g at 400 °C to 0.011974 cm³/g at 900 °C. This change of pore structure can also be observed from SEM images, as shown in Figure 5.

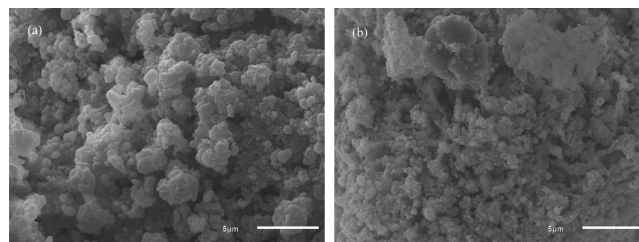


Figure 5. SEM images of precalcined CaO-CuO-MgO composites after oxidation. Precalcination was carried out at (a) 400 °C, and (b) 900 °C during composite fabrication process.

It seems that the distribution of Cu/CuO on the surface of CaO could generate a higher resistance for the subsequent carbonation of CaO, and finally leads to the observed decay of CO₂ sorption. Moreover, precalcination at high temperature, especially >800 °C, could further intensify this kind of “wrapping” effect, which was probably caused by the low melting point of Cu (1084 °C) and CuO (1336 °C).³² It is well-known that CaCO₃ can reduce the melting point of minerals and it would further reduce the melting point of Cu/CuO which covers the surface of CaO and reduces the carbonation reaction rate. However, it appears that all of the calcium in the composite is still available for reaction. A prolonged carbonation of CaO-CuO-MgO, which was precalcined at 900 °C for 1.5 h during fabrication, was carried out after 2 cycles under the following conditions: calcination/reduction in 15% CH₄ at 800 °C for 10 min, oxidation in air and carbonation in 15% CO₂, both at 650 °C for 10 min, with the results shown in Figure 6. Although it only shows a

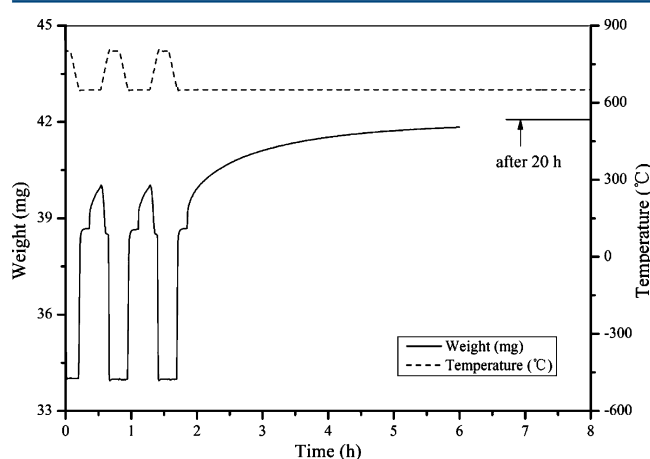


Figure 6. The prolonged carbonation of CaO-CuO-MgO, which was precalcined at 900 °C for 1.5 h in advance before the following test: calcination/reduction in 15% CH₄ at 800 °C for 10 min (20 h at the 3th carbonation), oxidation in air and carbonation in 15% CO₂, both at 650 °C for 10 min.

carbonation conversion of 38% after carbonated for 10 min in the third carbonation, when this process was prolonged to 20 h, a conversion of around 98% was demonstrated. Although it is not very clear how exactly Cu/CuO reduces the carbonation rate, it does not prevent the reaction from proceeding to the end. This could be because the “wrapping” of Cu/CuO on the surface of CaO is only local and thus calcium can still diffuse to the outer surface for further carbonation reaction.

3.3. Effect of Operating Temperatures. Operating temperature has been proved to be an important parameter for the activity of CaO-based sorbents in calcium looping and CuO-based oxygen carriers in chemical looping combustion. Moreover, high temperature would aggravate the negative influence of Cu/CuO on the uptake of CaO, as shown in previous section. Therefore, in this part, the effect of operating temperature during the reactions of calcinations/reduction, oxidation and carbonation were investigated using the 400 °C precalcined CaO-CuO-MgO.

Figure 7 shows that the reactivity of CaO and Cu as a function of oxidation and carbonation temperature. Here, calcination/reduction conditions were fixed at 800 °C for duration of 10 min, and oxidation and carbonation temperature

were kept the same but varied from 600 to 800 °C. The reactivity of Cu seems to be insensitive to the oxidation and carbonation temperature, because above 95% of oxidation conversions were always observed, regardless of temperature change. In contrast, high temperature was found to be more beneficial for the carbonation of CaO. Furthermore, with increasing temperature, there is a slower reactivity loss with increasing number of calcination/reduction, oxidation and carbonation cycles when temperature is not higher than 750 °C. When the composite was carbonated at 800 °C, decomposition was dominant in the reversible reactions and no CaCO₃ could be formed after 10 min.

The influence of calcination/reduction temperature on the reactivity of CaO and Cu in the composite was also investigated. It seems that regeneration of the composite should not be a barrier in the new CaCuCL process, because the decomposition of CaCO₃ and reduction of CuO were always fast and complete, and no distinguishable difference in reaction rate could be found in the whole temperature range studied. The reactivity of Cu during oxidation is stable as well. However, lower temperature is preferable for the carbonation of CaO in composite and this trend is prominent between 800 and 950 °C, as shown in Figure 8. Taking the requirement of complete decomposition of CaCO₃ in CO₂ atmosphere into consideration, the temperature of calcination/reduction should be at around 800–850 °C.

3.4. Long-Cycle Performance of Different Composites.

In this part, three CaO/CuO/MgO composites were synthesized with different techniques and then tested for their reactivity in 68 cycles of successive reactions containing calcination/reduction, oxidation and carbonation. Besides wet mixing described above, sol-gel technique^{34,35} and mechanical mixing method were adopted here to prepare sorbents. It should be noted that the three composites were synthesized from the same precursors with identical composition in order to explore the potential effect of preparation methods. For sol-gel technique, first, calculated amounts of calcium acetate, copper acetate, magnesium acetate, and citric acetate were added into distilled water with the molar ratio of water to metal ions of 50:1 and citric acid to metal ions of 1:1. Subsequently, the mixture was vigorously stirred at 80 °C for around 7 h to get well dispersed sol. The sol was then placed at room temperature for 18 h to form wet gel. The sample was finally obtained after the processes of overnight drying at 110 and 400 °C calcination for 1.5 h. For mechanical mixing, it was achieved by ball milling of calcium acetate, copper acetate and magnesium acetate together for 10 min.

The three synthetic samples were tested for 68 cycles in the thermogravimetric analyzer using the previously determined optimum operating parameters: 800 °C for calcination/reduction, and 750 °C for oxidation and carbonation, and the results are shown in Figure 9. The reactivity and stability of Cu is excellent, around 94% in the whole 68 cycles, for all the synthetic composites, though a little difference was observed of their trends during the 68-cycle testing. A slow decrease of the oxidation conversion followed by an increase was demonstrated for the wet mixed composite. For Sol-Gel composite, the oxidation conversion of Cu gradually increased during the whole process, while an opposite trend was found for the sorbent synthesized by mechanical mixing. With regards to the reactivity of CaO in the sorbents, all of the synthetic composites demonstrated a continuous loss of the CO₂ sorption capacity. For instance, a carbonation conversion of

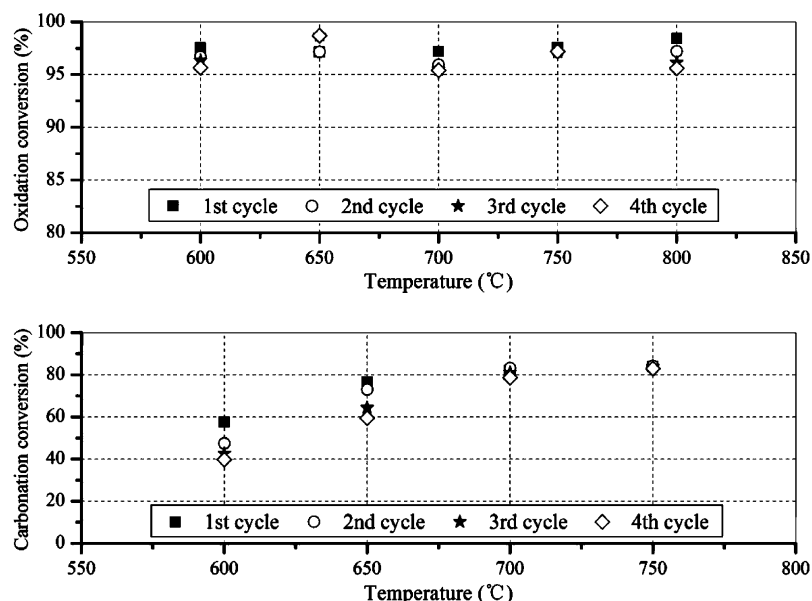


Figure 7. The oxidation and carbonation conversion of CaO-CuO-MgO under different oxidation and carbonation temperatures for 4 cycles. Testing conditions: calcination/reduction in 15% CH₄ at 800 °C for 10 min, oxidation in air and carbonation in 15% CO₂, both for 10 min.

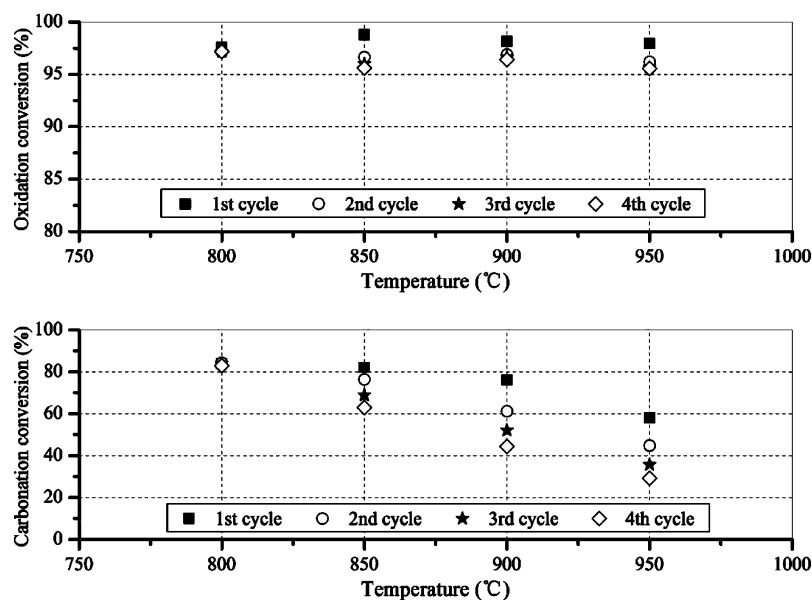


Figure 8. Effect of calcination/reduction temperature on the reactivity of CaO-CuO-MgO. Testing conditions: calcination/reduction in 15% CH₄ for 10 min, oxidation in air and carbonation in 15% CO₂, both at 750 °C for 10 min.

83.7% can be observed for the composite synthesized by mechanical mixing in the first cycle, however, only a value of 18.7% can be found after 68 cycles. The changes in the carbonation conversion of the other two composites with the number of cycle were very similar and the conversions were always higher than the mechanical mixed sorbent, but the final conversion became only 27% after 68 cycles. Apparently, the samples tested in the work all exhibited severe instability on the CO₂ uptake with the number of cycles, and this poor performance was the main technical problem for the cyclic utilization of CaO/CuO based materials in the real combined calcium and copper chemical looping process.

3.5. Discussion. The performance of CaO/CuO based composite observed in this work clearly demonstrates that it is technically feasible to develop a combined calcium and copper

chemical looping (CaCuCL) for postcombustion CO₂ capture. Excellent reduction and oxidation reactivity of Cu/CuO has been found in a wide range of temperatures with satisfactory reaction rates, also the reactivity of the two reactions is stable during 68 cycles. The major problem is still the loss-in-capacity of CaO, which seems to be severer in the CaO/CuO based composite, comparing to the sorbents used for typical calcium looping cycles, because of the observed negative influence of Cu/CuO on CaO. It should be noted that in the conventional calcium looping, after a limited number of carbonation and calcination cycles, the low-reactivity CaO could be used as raw material in cement production from the cheap, abundant and environmentally benign limestone and dolomite precursors.³⁶ However, in the new proposed CaCuCL, the composite is mainly composed of expensive CuO, which should be cyclically

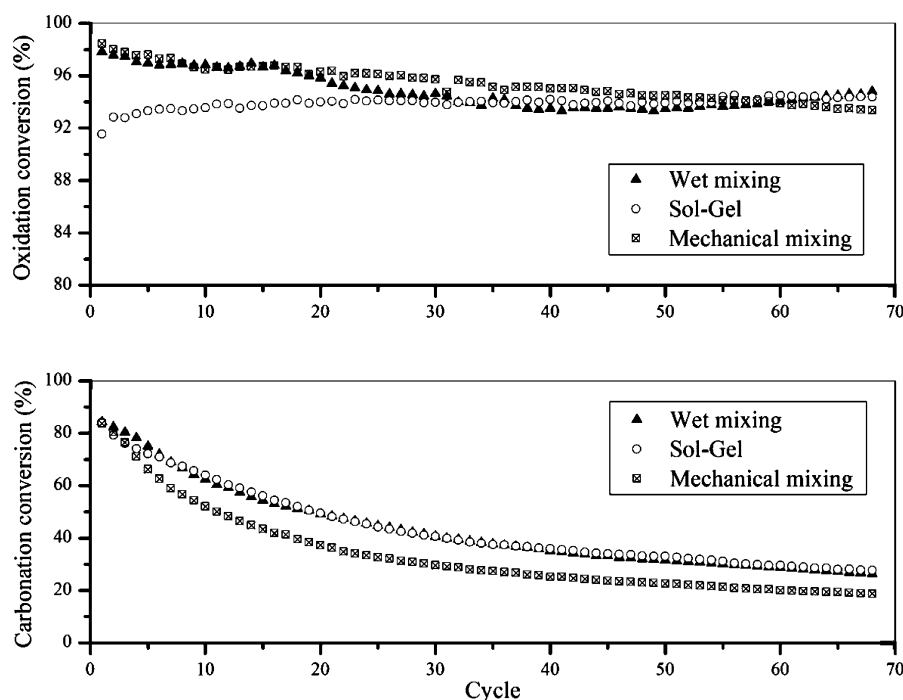


Figure 9. Cyclic reactivity of CaO-CuO-MgO composites fabricated with different methods for 68 cycles. Testing conditions: calcination/reduction in 15% CH₄ at 800 °C for 10 min, oxidation in air and carbonation in 15% CO₂, both at 750 °C for 10 min.

used for a much longer time. Otherwise the loss of composite would greatly increase the cost and reduce the economic benefits of CaCuCL. So the loss-in-capacity of CaO in the CaO/CuO based composite is a problem that must be addressed.

The specific energy requirement during the calcination/reduction process of the new CaCuCL process determines that there should be a much lower fraction of CaO in the CaO/CuO based composite compared to CaO-based sorbents used for typical calcium looping. In this case, some methods like wet impregnation,³⁷ which has been proven to be effective to overcome the problem of loss-in-capacity but limited by the relatively low content of CaO in the synthetic sorbents, would be useful for the fabrication of CaO/CuO based composite.

It should be noted that the sorbents tested here are all in the form of fine power. For real applications in fluidized bed or fixed bed, the sorbents should be fabricated in the form of particles with an acceptable mechanical strength before it can be used. However, in this case the chemical reaction rates of the sorbents would change, usually becoming slower than that when in powder form.

4. CONCLUSIONS

An experimental study of the performance of synthetic CaO/CuO/MgO in a combined calcium and copper chemical looping process has been carried out. It was found that the sorbent can be regenerated easily and readily for the next reactions. However, a significant resistance for the carbonation of CaO was observed when Cu/CuO was added into the composite. This negative effect was thought to be due to the “wrapping” of Cu/CuO on the outer surface of CaO. With the help of SEM and TGA, the morphology change has been observed and the assumption was proved by the prolonged carbonation for 20 h. It is also suggested that when calcined/

reduced at 800 °C, and oxidated and carbonated at 750 °C, the synthesized composite has the best reactivity and stability.

■ ASSOCIATED CONTENT

Supporting Information

X-ray diffraction patterns of CaO-CuO-MgO after each reaction, mass curve of synthetic CaO/CuO/MgO in successive reactions, and effect of mass in TGA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +61-7-33469193. Fax: +61-7-33654799. E-mail: b.feng@uq.edu.au.

Notes

The authors declare no competing financial interest.

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