DEMONSTRATING CO_2 CAPTURE AND IN SITU UTILIZATION TOWARD SYNGAS PRODUCTION IN A CARBONATE LOOPING PROCESS COUPLED WITH DRY CH_4 REFORMING

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ABSTRACT

Combining $CaCO_3$ calcination with dry reforming of CH_4 in a single, reactive separation step can bring several benefits to the incumbent calcium looping process, by enabling operation at milder temperatures and simultaneous production of syngas. This work provides the experimental proof-of-concept of the intensified calcium looping process over a bifunctional material that combines both CO_2 capture and reforming activities. Coupling $CaCO_3$ calcination with dry CH_4 reforming was demonstrated in a lab-scale unit equipped with a fluidized bed reactor, while a parametric evaluation for the integrated calcination step was performed, by varying main operating conditions. Applying a CH_4 flow enabled rapid $CaCO_3$ decomposition even at low temperatures (625-750 °C) compared to inert flow, since the *in-situ* CO_2 consumption enhanced the calcination driving force. At 700 °C syngas production with a stable H_2/CO ratio close to 1 was achieved, until the complete calcination of the material. The *in-situ* consumption of the released CO_2 enabled complete calcination even at 625 °C, while leading up to 80% CO_2 utilization.

KEYWORDS: Calcium looping; Integrated CO_2 capture and utilization, CH_4 dry reforming, Bifunctional material, Syngas production

INTRODUCTION

Extensive use of fossil fuels has led to increased CO_2 emissions, with energy intensive industries and large power plants contributing to more than 60% of the global emissions [1]. This has led to CO_2 concentrations far above pre-industrial levels, which is considered the main contributing factor to global warming. In this context, it is necessary to reduce the CO_2 emissions and mitigate their negative effect. At this direction, research efforts are focused on developing processes for CO_2 capture from industrial flue gas but also as a means for intensification of thermodynamically limited processes such as steam methane reforming [2-4]. Calcium Looping (CaL) is a promising CO_2 capture scheme based on the carbonation of CaO at temperatures ranging between 600-700 °C and the subsequent calcination of the formed $CaCO_3$ at higher temperatures (≥900 °C), to release the captured CO_2 [5]. The main challenges of this process concern the harsh operating conditions and energy demand of the periodic calcination stage. Coupling CaL with direct utilization of the released CO_2 has the potential of mediating the operating conditions [6-8], which can be achieved by using a reactive gas feedstock, such as CH_4, in the calcination stage [9,10]. The calcination-released CO_2 can be converted to syngas via the dry reforming of CH_4 (DRM), while the in-situ utilization of CO_2 can intensify the calcination stage and enable its conduction at lower temperatures (650-700 °C), according to *Le Chatelier's* principle. This approach contributes to the mitigation of CO_2 emissions, by *in–situ* upcycling CO_2 to generate syngas, an important building block used for a broad range of chemicals and fuels.

Keystone for the integration of calcium looping with DRM is the development of bifunctional materials with high CO_2 capture capacity and catalytic activity for dry reforming. This study investigated a candidate bifunctional material for providing the experimental proof of concept of the

intensified process, combined with a detailed parametric analysis of the main operating conditions.

EXPERIMENTAL

Material synthesis

A NiO/CaO-based bifunctional material (BFM) with 10wt% NiO, 60wt% CaO and 30wt% $CaZrO_3$ nominal composition was synthesized via a sol-gel auto-combustion method [11]. The procedure comprised of mixing the precursors and the combustion agent (citric acid) in distilled water, followed by water evaporation. The formed gel was auto combusted at 300 °C in a furnace and the final powder was calcined under air flow for 1.5 h at 850 °C. The developed BFM was denoted $Ca_{60}Ni_{10}Zr_{30}$.

Experimental proof-of-concept in fixed & fluid bed reactor

Coupling $CaCO_3$ calcination and CH_4 dry reforming for syngas generation was experimentally proven over the developed Ni/CaO material in a lab-scale unit with fixed or fluidized bed configuration. The BFM was initially exposed under pure Ar flow from 25 to 800 °C to release CO_2 and H_2O captured from the atmosphere. After cooling the reactor to 650 °C, the material was reduced by 10 vol% H_2/Ar and the carbonation step followed by switching to a 10 vol% CO_2/Ar flow. Once the material approached saturation, the feed was switched to a CH_4/Ar flow to conduct the calcination/DRM step.

Parametric analysis

The performance of the BFM was also evaluated by investigating the effect of the main conditions of the intensified calcination/DRM step when conducted in the fluidized bed reactor. The main parameters evaluated include temperature (625-750 °C) and CH_4 concentration in feed (3-10 vol%).

RESULTS AND DISCUSSION

Typical profiles of the reactor's exit stream during a carbonation and calcination/DRM cycle are presented in Figure. 1a & 1b for the experiments performed in the fluidized and fixed bed reactor respectively. During the first stage, as carbonation reaction occurred, only a small fraction of CO_2 was detected at the exit of the reactor. The outlet CO_2 partial pressure was stable and close to that predicted by the equilibrium at 650 °C (~1%) for both reactor configurations. Prior reaching saturation in CO_2, the feed was switched to 3 vol% CH_4/Ar to carry out the calcination/DRM stage. As $CaCO_3$ gradually decomposed, the CO_2 released reacted with CH_4 toward syngas via DRM with a constant H_2/CO ratio close to 1 (Figure 1a). When calcination reached completion, a transitional period followed (2nd regime) where mainly CH_4 decomposition took place and finally when the material's surface was blocked by the solid C, CH_4 cracking was also restrained (3rd regime). These regimes could not be clearly distinguished in the experiment with the fixed bed (Figure 1b), where the reactor profile revealed a transient response of the H_2, CO and CO_2 signals. This is attributed to the shift of the reaction front along the material bed in the axial direction and the alteration over time of the types of reactions occurring at different parts of the bed, as shown in the inset of the figure. Initially, the inlet CH_4 would be consumed in the upper parts of the reactor via the DRM reaction, while the produced H_2 would also react with the CO_2 released from $CaCO_3$ decomposition in the lower layers via the RWGS reaction. This resulted in the generation of syngas with a H_2/CO ratio lower than 1 during the 1st regime, followed, however, by the gradual increase of the H_2 signal and the decrease of the CO signal (2nd regime). This is attributed to the unavailability of $CaCO_3$ at the upper parts of the reactor with time, thus enhancing CH_4 decomposition. This in turn results in much less CH_4 available for syngas production at the lower layers, where $CaCO_3$ would still be present. During the 3rd regime, CH_4 and H_2 followed similar upward and downward trends respectively with the experiment performed in the fluidized bed reactor.
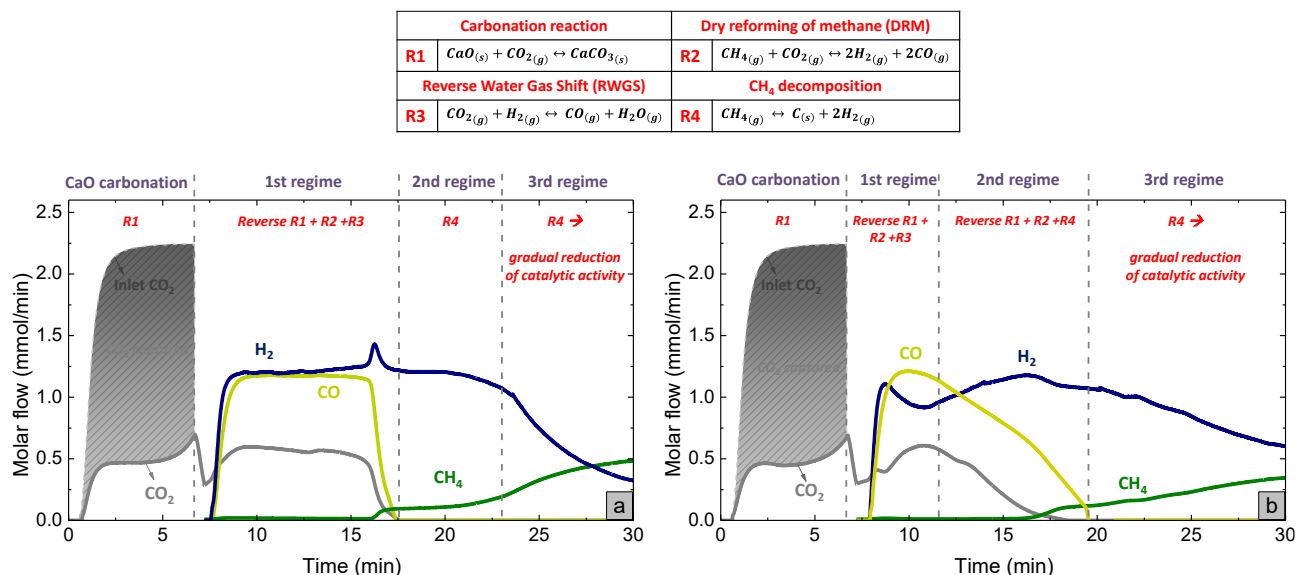
	Carbonation reaction		Dry reforming of methane (DRM)
R1	$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)}$	R2	$CH_{4(g)} + CO_{2(g)} \leftrightarrow 2H_{2(g)} + 2CO_{(g)}$
	Reverse Water Gas Shift (RWGS)		CH₄ decomposition
R3	$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)}$	R4	$CH_{4(g)} \leftrightarrow C_{(s)} + 2H_{2(g)}$

Figure 1. *Gas products evolution during the calcium looping coupled with DRM experiments in a fluidized (a) and a fixed bed reactor (b) (carbonation: T=650 °C, , 10vol% CO_2/Ar, calcination/DRM: T=700 °C, , 3vol% CH_4/Ar, W/F = 3 g min/l).*

The operating conditions of calcination/DRM stage, which include temperature and CH_4 concentration were investigated experimentally over the $Ca_{60}Ni_{10}Zr_{30}$ BFM. Temperature comprised a decisive parameter, with lower values enabling high CO_2 conversion (~80% at 625 °C – Table 1) while generating syngas with stable H_2/CO ratio. However, the $CaCO_3$ decomposition proceeded with slower rate and thus, due to the lower availability of CO_2, part of CH_4 was selectively consumed via its decomposition toward H_2 and C as confirmed by the H_2/CO ratio higher than 1. DRM and CH_4 decomposition also displayed lower reaction rates, as implied by the lower CH_4 conversion (~82%) compared to the higher temperatures, with CH_4 reaching almost complete conversion (~97 %) when increasing the temperature to 650 °C. Despite the increase of CH_4 conversion, the *in–situ* CO_2 utilization degree demonstrated the opposite trend with higher temperatures, as the CO_2 partial pressure approached equilibrium partial pressure of calcination reaction for each temperature.

Table 1. *Effect of temperature during calcination/DRM stage on H_2/CO molar ratio, CH_4 conversion and in-situ CO_2 utilization.*

Temperature (°C)	H₂/CO ratio (-)	CH₄ conversion (%)	CO₂ utilization (%)
625	1.29	81.6	79.8
650	1.20	92.9	76.0
675	1.15	97.0	62.6
700	0.94	97.1	54.0
725	0.78	97.4	42.7
750	0.57	98.0	23.6

Another important operating condition of the integrated calcination stage is the concentration of CH_4 in the gas feedstock. To study the effect of this parameter, isothermal experiments were performed at 650 °C, by varying the CH_4 concentration in the feed (3, 5 and 10%). Figure 2a presents the effect of CH_4 content on CH_4 conversion, *in–situ* CO_2 utilization and H_2/CO ratio of the generated

syngas. Increase of CH_4 concentration resulted to a slightly higher *in–situ* CO_2 utilization efficiency with a simultaneous decrease in CH_4 conversion and increase of H_2/CO ratio.

To better understand the behaviour of the CO_2 utilization efficiency, Figure 2b displays the $CaCO_3$ decomposition and CH_4 consumption rates as a function of time for the experiments performed at the three different CH_4 concentrations. For comparison, $CaCO_3$ decomposition rate when conducting calcination under inert Ar flow is also provided. CO_2 released from $CaCO_3$ decomposition, can either stay adsorbed on active sites and react with activated CH_4 or desorb in the gas phase. Increasing CH_4 in the gas feed enables a higher consumption rate of CO_2 available on active sites toward syngas production. However, the higher CH_4 inlet content and thus higher syngas flow increase the total volumetric flow and thus decrease the CO_2 partial pressure. This promotes the desorption rate of CO_2 in the gas phase in order to reach the CO_2 equilibrium partial pressure. Both consumption and desorption aspects enhance the driving force of $CaCO_3$ decomposition, significantly reducing the duration of the calcination/DRM stage. The higher in situ CO_2 utilization degree with increasing CH_4 concentration indicates that the increase of the consumption rate is higher than the increase of desorption rate.
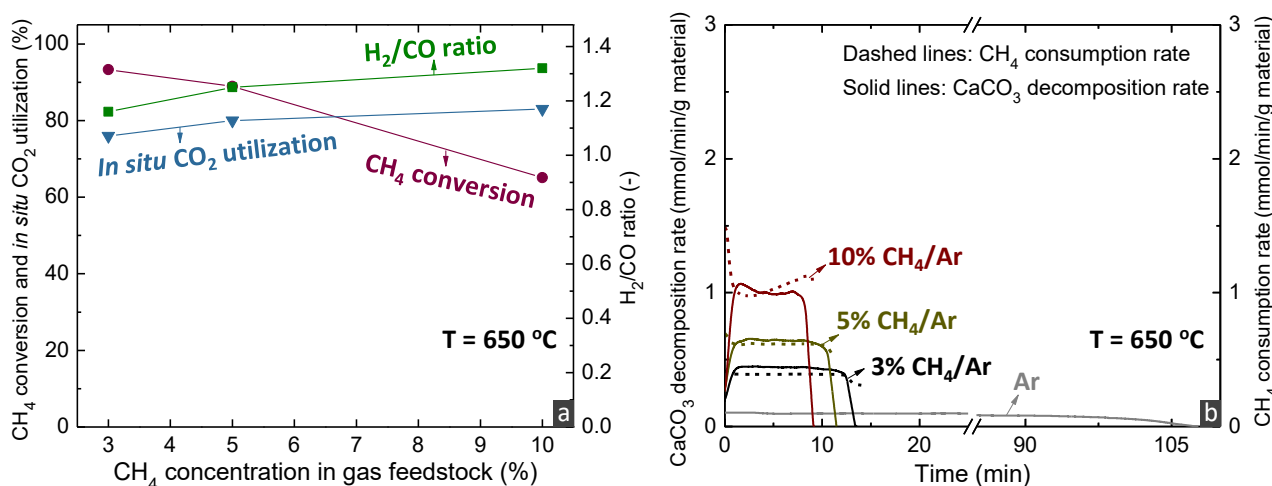

Figure 2. *CH_4 conversion, in–situ CO_2 utilization, H_2/CO ratio of syngas (a), and $CaCO_3$ decomposition and CH_4 consumption rates over time as a function of CH_4 concentration during the calcination/DRM stage in a fluidized bed reactor (T=650 °C, W/F = 3 g min/l)*

The stability of the $Ca_{60}Ni_{10}Zr_{30}$ BFM was examined for 20 consecutive cycles of carbonation and calcination/DRM. An isothermal experiment at 650 °C and an additional experiment where temperature was alternating between 650 and 700 °C for carbonation and calcination/DRM stage were performed (Figure 3). The material demonstrated high stability in terms of in situ CO_2 utilization and catalytic activity as indicated by the constantly high CH_4 conversion and the stable H_2/CO ratio of the generated syngas. However, the CO_2 capture capacity during carbonation declined by ~22% during the isothermal test, while the loss was even higher (47.0%) with the higher calcination temperature of 700 °C.

Although CH_4 decomposition was inevitable due to the relatively low temperatures (650–700 °C), the formed carbon could be partially gasified from CO_2 during the subsequent carbonation stage, allowing for stable catalytic reforming activity for 20 cycles. Post-reaction characterization with TPO showed that only a small amount of carbon is accumulated on the BFM surface over 20 cycles (0.015-0.025 mol C/mol of $CH_{4,in}$), with the higher temperature applied (700 versus 650 °C) exhibiting lower C deposition.
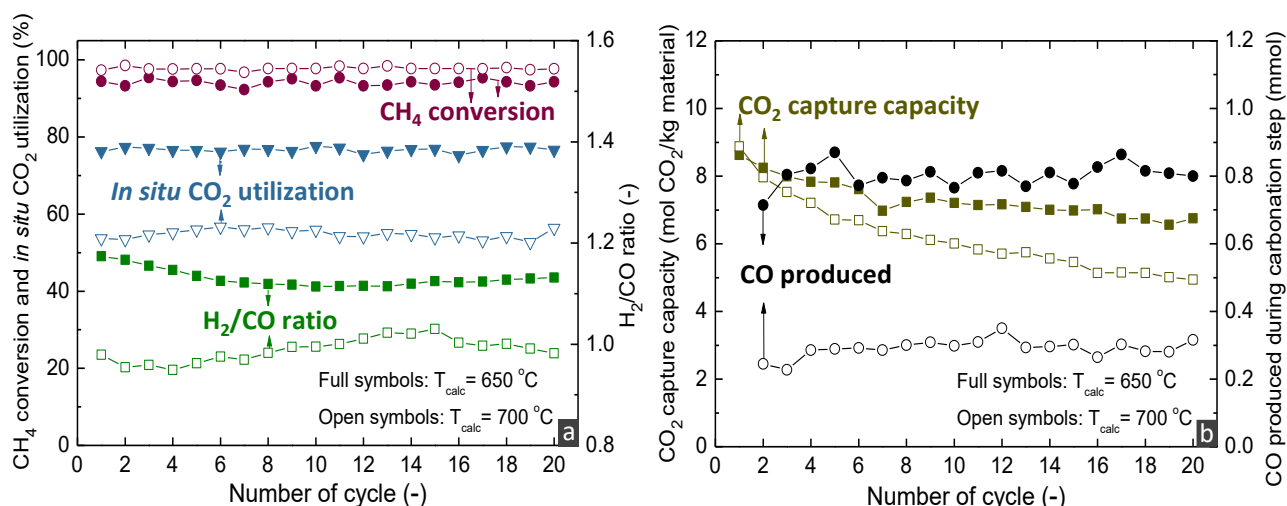
Figure 3. *CH₄ conversion, in–situ CO₂ utilization, H₂/CO ratio of syngas during the calcination/DRM stage (a), and CO₂ capture capacity and CO produced during the carbonation stage (b) for 20 consecutive cycles in a fluidized bed reactor (carbonation: T=650 °C, 10vol% CO₂/Ar; calcination/DRM: T=650 or 700 °C, 3vol% CH₄/Ar)*

CONCLUSIONS

Combining $CaCO_3$ calcination with DRM in a single step allows operating at milder temperatures while generating syngas with a H_2/CO ratio close to 1. The beneficial effect was more pronounced in fluidized bed reactor since the uniform mixing of inlet CH_4 and solid particles throughout the material bed contributed to the generation of syngas with stable H_2/CO ratio over time. The in-situ consumption of the released CO_2 enables complete calcination even at 625 °C, while leading up to 80% CO_2 utilization. Increasing the CH_4 concentration in the feed led to higher CO_2 consumption rate compared to CO_2 desorption rate, while the CH_4 conversion and H_2/CO ratio of produced syngas were retained stable for a range of CH_4 concentrations. The bifunctional material showed a stable catalytic activity for 20 consecutive cycles due to the low accumulation of carbon on the surface, since carbon was partially gasified from CO_2 during the subsequent carbonation stage in each cycle.

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