

EXPERIMENTAL INVESTIGATION ON A NOVEL COMBINED CHEMICAL LOOPING REFORMING PROCESS

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ABSTRACT

CO₂ capture and utilization (CCU) technology has been widely adopted to reduce the greenhouse effect. The emerging chemical looping technology applied in the syngas production and gas-solid separation process has attracted widespread attention. In this research, a novel combined chemical looping reforming (CLR) process with CCU is realized in one system with CaO and Fe₂O₃ as the CO₂ and oxygen carriers, respectively. The effects of operating parameters (i.e. Fe₂O₃/Al₂O₃ weight ratio, CO₂ carrier feed ratio, CH₄ feed concentration and reforming temperature) on the reforming performance are investigated through the experiments in a fixed bed reactor. The results show that these operating factors have significant impacts on the reforming reactivity. 2.5 times of CaCO₃ simulation amount has the lowest CO₂ releasing, 60wt% Fe/Al material obtains the highest H₂ and syngas yields, 4.5% CH₄ is beneficial for maintaining higher and more stable CH₄ conversion and syngas purity, and 850°C seems to be more suitable for combined CLR. The interaction between oxygen carrier and CO₂ carrier is identified and discussed. The optimization for the operating conditions of this combined CLR process would provide an alternate pathway for efficient and clean syngas production.

Keywords: CO₂ capture and utilization, chemical looping reforming, CO₂ carriers, oxygen carriers, syngas production, energy savings

1. INTRODUCTION

With the rapid increment of CO₂ content in the atmosphere, harmful damage to the environment caused by the greenhouse effect is becoming more and more serious. Many effective CO₂ capture and

utilization (CCU) methods have been proposed to deal with this problem^[1]. For CO₂ capture, pre-combustion, post-combustion and oxy-fuel combustion technologies^[2, 3] can be employed. Among many CO₂ utilization methods, CO₂-CH₄ dry reforming for syngas production, as shown in Equation (1), has attracted great attentions due to its fast reaction rate and simultaneous usage of methane and carbon dioxide^[4]. However, the direct gas-gas reaction and fast reaction rate might bring potential issues of the difficult product purification and reaction process control. Fortunately, chemical looping technology, which can separate one reaction into two or more separated reactions, can effectively solve the above issues via the solid material circulation, gas-solid reaction and inherent separation.

Although great achievements have been obtained for these CO₂ capture and CO₂ utilization approaches, the way to better connect them is still lacked. Therefore, several attempts have been conducted. Firstly, as an approximate idea, a Ca-Cu looping process was proposed for H₂ production with CO₂ capture, where CaO was used as CO₂ sorbent to realize sorption enhanced H₂ production while the Cu-based chemical looping combustion was employed to supply heat for the extensively endothermic calcination reaction (i.e. Equation (2))^[5, 6]. However, in this process, CO₂ utilization is not considered, the captured CO₂ needs further treatment, and fuel gas utilization efficiency is relatively low. In order to solve these issues, in our previous work^[7], a novel combined chemical looping reforming process (Fig 1) for syngas production was proposed and the integration of CO₂ capture and utilization in one system was achieved. This novel combined chemical looping system obtained significant improvements on not only the integrated CCU but also the desired product with flexible H₂/CO ratios based on

the adjustable feed amount of O₂ and CO₂ sources. Thermodynamic calculation and process simulation demonstrated that the desirable solid materials can be screened out and the external heat demands can be much lower than that of the traditional dry reforming process. Moreover, from the preliminary lab-scale experiment performed on a fixed-bed reactor with CaO and Fe₂O₃ (mole ratio 0.15:0.8) as the CO₂ carrier and O₂ carrier, respectively, the gas product content and the crystal compositions before and after reforming reactions confirmed the feasibility of this novel concept and identified the potential cyclic performance of the process.

Based on the previous attempts, in this study, a comprehensive experimental investigation is conducted to manifest the reforming reaction performance, to optimize the operating conditions and to discuss the interaction between oxygen and CO₂ carriers for this novel combined chemical looping process. Several key operating factors, including Fe₂O₃/Al₂O₃ weight ratio, the feed amount of the CO₂ carriers, the CH₄ feed concentration and reforming temperature, are studied to identify their effects on the CO₂ capture and syngas production.

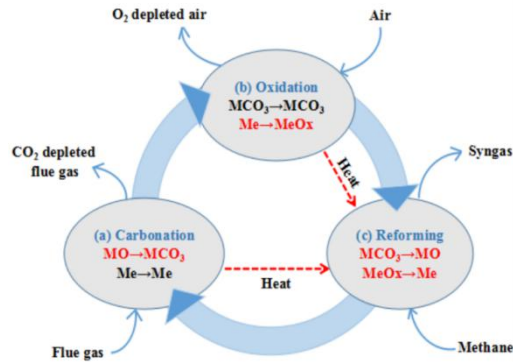
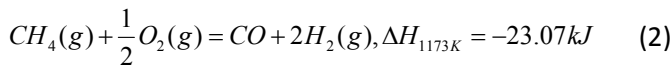
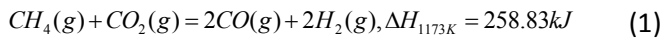


Fig 1 The novel combined chemical looping reforming process for syngas production^[7]

2. MATERIAL PREPARATION AND EXPERIMENTAL METHODS

Fe-based oxygen carriers were synthesized via a co-precipitation method^[8] with Al₂O₃ as the support. With the adjustment of the pH value at 9-10, ammonia was dropped into the mixed aqueous solution of Fe(NO₃)₃·9H₂O and Al(NO₃)₃·9H₂O to form precipitates. The obtained suspension was then put into the oven under 80°C overnight. The clay was then calcined in the

muffle furnace under 400°C for 3h, 600°C for 3h and 900°C for 6h. The reddish brown powder was finally mechanically mixed with CaCO₃ nano-powder (AR, Aladdin).

The 1g solid carrier was put inside the constant temperature zone of a stainless reactor tube (i.d. 12mm) with quartz cotton below. 4.5% CH₄ with total 100ml/min flow rate was introduced into the reactor and the flow rate was controlled by two mass flow-meters. The reforming reaction was performed at atmospheric pressure and the reaction tube was heated for 30min by the electronic furnace with two N-type thermocouples to reach the desired reforming temperature (600 to 950°C). Before the reforming reaction, 100ml/min 20% CO₂ was imported during the heating process to avoid CaCO₃ decomposition. After each reforming process, pure N₂ was blown into the tube to prevent the residual gases from affecting the next reaction. The oxidation and carbonation reactions both lasted for 2 hours under 600°C were carried out with 100ml/min 99.999% air and CO₂, respectively, to regenerate the carriers. All the reforming exhausted gases were detected by a gas chromatography.

Polycrystalline X-ray diffraction (XRD) and CO₂ gas analyzer (GSS detector) were applied for the detection of crystal phase change before and after reactions and the response value of CO₂ in the exhaust gas, respectively. Besides, the gas concentration distribution was displayed for a certain reaction process. CH₄ conversion rate (γ_{CH_4}) and syngas purity (P_{syn}) were calculated according to Equations (3) and (4) to evaluate the material reactivity.

$$\gamma_{CH_4} = \frac{n_{CH_4,in} - n_{CH_4,out}}{n_{CH_4,in}} * 100\% \quad (3)$$

$$P_{syn} = \frac{n_{H_2} + n_{CO}}{n_{H_2} + n_{CO} + n_{CO_2} + n_{CH_4,out}} * 100\% \quad (4)$$

3. RESULTS AND DISCUSSION

3.1 Effect of CaCO₃ amount

To explore the influence caused by the amount of CO₂ carriers, CaCO₃ with different times of the simulation amounts^[7] were tested and the CO₂ concentration emitted from reforming processes was shown in Fig 2(a). The four curves have the same tendency that CO₂ contents first keep constant subsequently with a small increment and then decrease. The decrement is related to that no more CO₂

is introduced to the reactor, while the small increment can be attributed to the decomposition of CaCO_3 . As shown in Fig 2 (b), H_2 concentration with simulation amount exhibited the most obvious first increase and then decrease trend, which might be related to the first exposure of the reaction site and the gradual consumption of the active substance. Meanwhile, the CH_4 conversion rate with simulation amount in Fig 2 (c) showed the most stable conversion stage in the later period despite the decrement in the former stage caused by the long residence time. Considering the experiment results mentioned above, CaCO_3 with simulation amount was chosen to fit the process requirement.

due to the loss of lattice oxygen in the Fe-based oxygen carriers. Besides, extremely no H_2 was generated at the

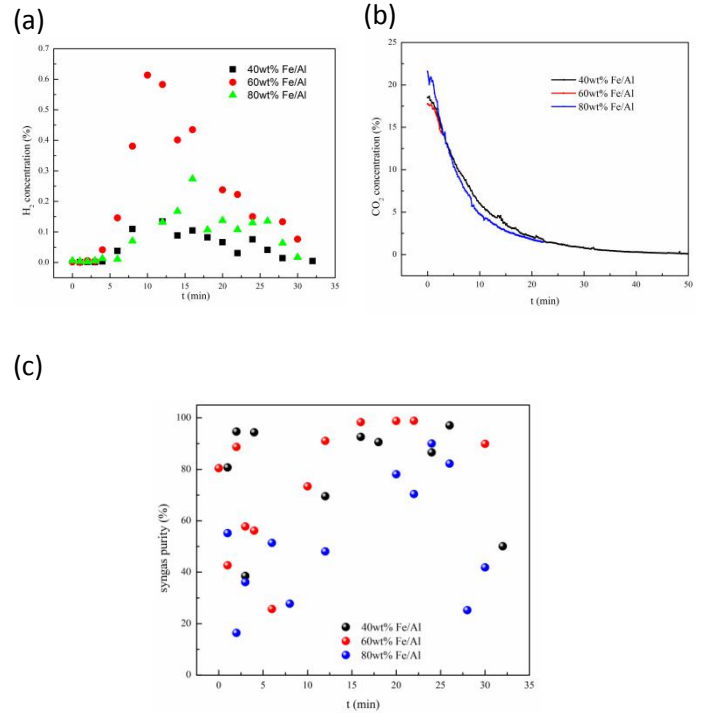


Fig 3 (a) H_2 concentration, (b) CO_2 concentration and (c) syngas purity varied with different Fe/Al ratio (40wt%, 60wt% and 80wt%) during the reforming process under 900°C

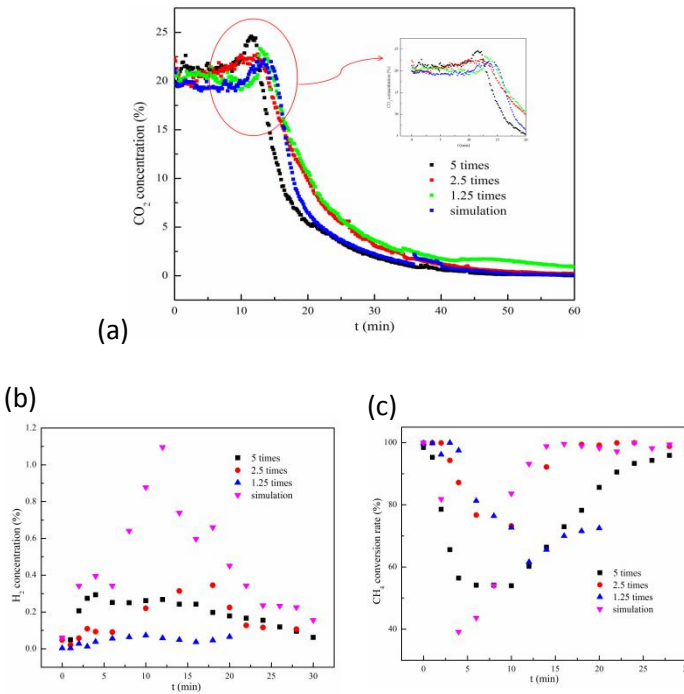


Fig 2 (a) CO_2 concentration, (b) H_2 concentration and (c) CH_4 conversion rate with different CaCO_3 feed amounts during the reforming process under 900°C

3.2 Effect of Fe/Al ratio

Oxygen carriers with the Fe/Al ratios of 40wt%, 60wt% and 80wt% were prepared to illustrate the impacts of active component on the reforming reaction performance. Fig 3 shows the instantaneous variations of H_2 concentration, CO_2 concentration and syngas purity. It was clearly seen from Fig 3(a) that H_2 concentration showed a trend of increasing first and then decreasing, concerning with the material reaction rate and the stoichiometric ratio of CH_4/FeOx increment

early stage indicates that the fast $\text{Fe}_2\text{O}_3\text{-CH}_4$ full-oxidation reaction is first occurred. As shown in Fig 3(b), it proved a negligible effect from the variation of Fe/Al ratios for CO_2 concentration during the reforming process. Moreover, it also illustrated that the CO_2 produced by the complete oxidation reforming in the early stage of the reforming process or other side reactions to generate CO_2 would not significantly affect the CO_2 protection atmosphere in the process. Since 60wt% Fe/Al case showed the highest H_2 concentration and syngas purity, it implies that the evolutions of H_2 concentration and syngas purity are concerned with the active substances and sites but totally not affected by CO_2 concentrations.

3.3 Effect of CH_4 concentration

As one of the most important reactants, the influence of CH_4 feed concentration on reforming reactivity needs to be explored. Fig 4 shows the variations of CH_4 conversion rate and syngas purity under the CH_4 concentration of 2.25% and 4.5%. It can be obviously seen that 4.5% CH_4 feed amount has a more constant and stable result in the later reforming

process even though the drastic decrease appeared in the early stage. It is ascribed to that the higher CH₄ concentration leads to such faster lattice oxygen consumption rate from solid carriers that the reactant gas would not effectively reacted. Fortunately, the minimum CH₄ conversion rate can reach to 90% and the maximum syngas purity is up to 100% with 4.5% CH₄. As shown in Fig 4 (a) and (b), the syngas purity curve tendency was almost consistent with that of CH₄ conversion rate, consistent with the findings in Ref. [9], owing to the H₂ product only derived from CH₄, and even though the CO product were originated from CH₄ and CaCO₃, because the amount of methane is much larger than that of CaCO₃, CH₄ also become the main CO source, thus explaining the consistent trends of the two parameters.

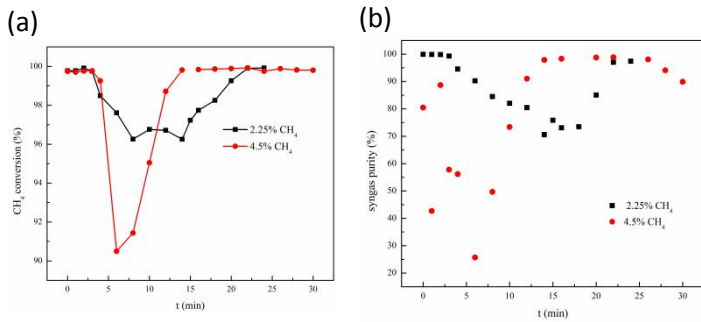


Fig 4 (a) CH₄ conversion rate and (b) syngas purity varied with different CH₄ concentration (2.25% and 4.5%) during the reforming process under 900°C

3.4 Effect of reforming temperature

Since this novel combined chemical looping process operates at atmosphere pressure, the impact of reaction temperature (i.e. 600°C to 950°C) on the product gas distribution is studied. Identical to that of other reforming influencing factors, CO₂ concentrations under different reforming temperatures appear with similar tendency as shown in Fig 5(d). This phenomenon shows that the effect of CO₂ on the process is consistent, which can better reflect the influence of the reaction temperature on the process results. Figs 5(a)-(c) indicate that high reaction temperature would be beneficial for syngas production and high CH₄ conversion. It can be seen from Fig 5(a) that H₂ concentration becomes higher when reforming temperature increases, because the endothermic CH₄ decomposition reaction is easier to occur at high temperatures. CH₄ concentration shown in Fig 5(c) also proved this result. As shown in Fig 5(b), steady CO is more likely to be obtained under 850°C.

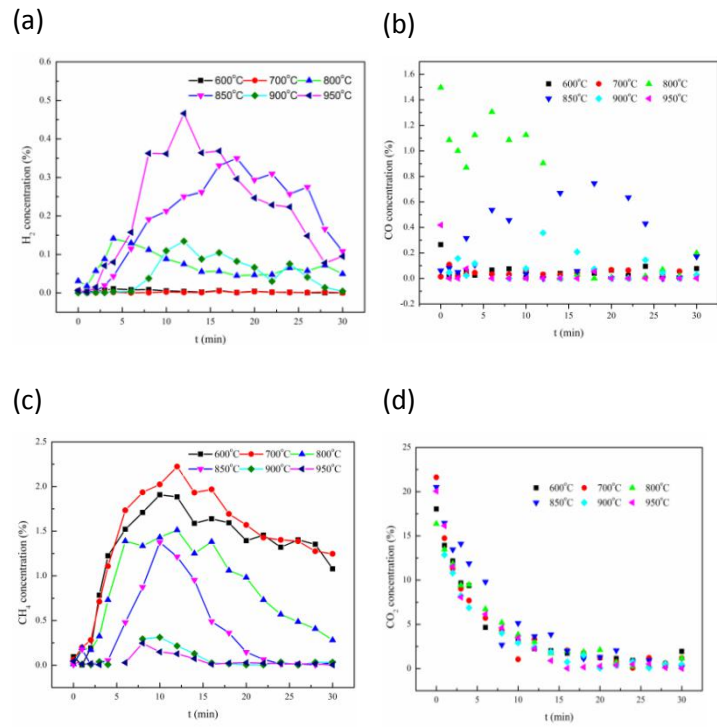


Fig 5 (a) H₂, (b) CO, (c) CH₄ and (d) CO₂ concentration varied with different temperatures from 600°C to 950°C during the reforming process

3.5 CO₂ atmosphere protection

Due to that CaCO₃ decomposition might be occurred during temperature ramping process, a fast ramping procedure (10 minutes) before reforming without CO₂ protection was carried out to manifest the impact of the protective CO₂ atmosphere on the reactivity. It can be clearly seen from Fig 6(c) the CH₄ conversion rate showed the same tendency and almost reached to 100% with and without CO₂ protection. Fig 6(a) to (c) illustrated that low CO₂ concentration was more conducive to H₂ generation since the reaction between CH₄ and excessive CO₂ was prone to produce H₂O and CO in the initial stage based on the Gibbs free energy minimization principle. The reforming process without CO₂ protection in Fig 6(b) showed that CO₂ generation in the combined chemical looping process was a multiple procedure based on the several stages of CO₂ concentration change. Further research needs to be carried out to explore the reaction mechanism.

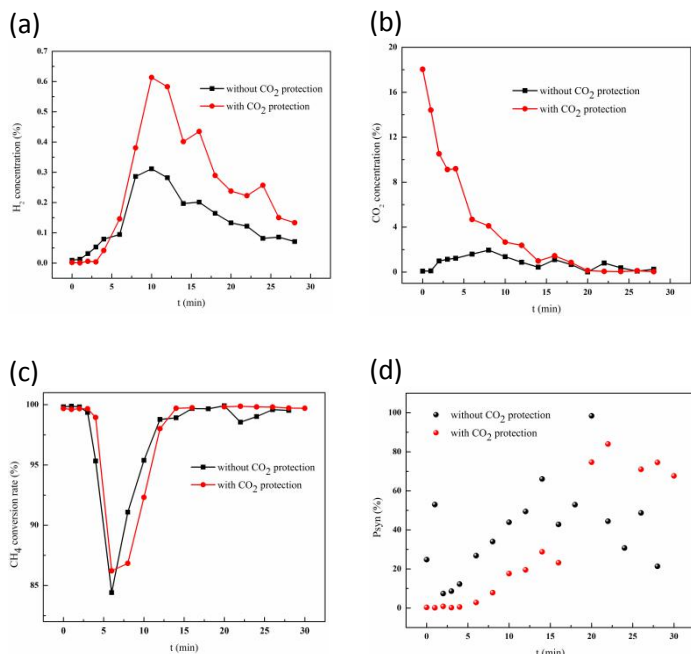


Fig 6 (a) H₂ and (b) CO₂ concentration, (c) CH₄ conversion rate and (d) syngas purity during the reforming process with and without CO₂ protection

3.6 Interaction between oxygen and CO₂ carries

As shown in Fig 7, the solid crystal composition was detected by XRD detector to further explore the interaction between CaCO₃ and Fe₂O₃/Al₂O₃ during the reforming process. CaCO₃ was changed into CaO with CO₂ releasing, Ca(OH)₂ was generated by a side reaction (CaO+H₂O→Ca(OH)₂ ΔG_{900°C}=-12.79kJ/mol), and CaCO₃ was remained because of the relatively low reforming rate or the CO₂ atmosphere existence in the CaCO₃-CH₄ single reforming. As for the Fe₂O₃-CH₄ single reforming, Fe₂O₃/ Al₂O₃ was partially reduced into Fe and spine FeAl₂O₄ because the lattice oxygen in the Fe₂O₃ cannot match the amount of methane reforming required that Fe-O-Al covalent substance was formed. Differently, in the combined chemical looping reforming, CaCO₃ was totally changed into CaO while Fe₃O₄ and FeO were detected. This phenomenon illustrated that the existence of Fe-based materials was beneficial for accelerating the CaCO₃ decomposition and Fe₂O₃ reduction degree was significantly slowed in the CO₂ atmosphere. In such way, the syngas generation period would be extended. Besides, the disappearance of spine FeAl₂O₄ in the combined chemical looping reforming suggested that the oxidative CO₂ might offer the oxygen atom for the Fe₂O₃-CH₄ reforming. Certainly, further

study should be conducted to uncover the reasons behind these reaction behaviors.

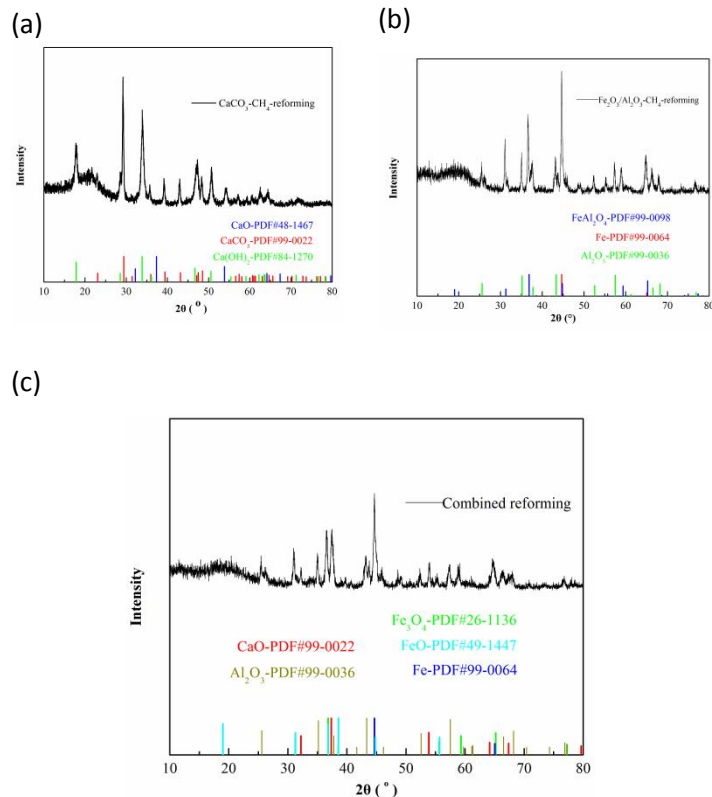


Fig 7 XRD results for solid carriers in (a) CaCO₃-CH₄ single reforming, (b) Fe₂O₃-CH₄ single reforming and (c) combined chemical looping reforming

3.7 Conclusions

The combined chemical looping reforming process uses the oxygen carrier and CO₂ carrier to supply lattice oxygen and CO₂ molecule to achieve an integrated CO₂ capture and CO₂ utilization in a single system. The effects of operating parameters on reforming reactivity are comprehensively investigated to obtain an optimal condition. CO₂ concentrations of all the reforming results show the same tendency and almost similar amount, whose impact can be eliminated, and thus the changes brought by other factors can be highlighted. It is found that nearly 100% syngas purity and CH₄ conversion rate can be reached when the 60wt% Fe/Al and 2.5 times of CaCO₃ simulation amount were put into the reactor under 900°C with 4.5% CH₄. An additional reforming process without CO₂ protection illustrated that lower CO₂ concentration was more beneficial for H₂ generation. XRD results had confirmed the interaction between CaCO₃ and Fe₂O₃ during the combined chemical looping reforming process. This

work would provide some useful and important information for getting further insight into the reaction performance of this novel combined chemical looping reforming process.

ACKNOWLEDGEMENT

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