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Thermodynamic analysis of a new chemical looping process for syngas production with simultaneous CO_2 capture and utilization

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ABSTRACT

Since typical CO_2 capture technologies lack the consideration of a reliable CO_2 storage method or integration with CO_2 utilization, this study proposes a new chemical looping reforming process for syngas production with simultaneous CO_2 capture and utilization. It integrates chemical looping, mixed reforming (i.e. CO_2 reforming and partial oxidation) and calcium looping using CO_2 carriers (CCs) and oxygen carriers (OCs). This novel process implements energy-efficient operation, attains flexible H_2/CO ratio, and captures CO_2 with immediate CO_2 conversion. Through thermodynamic screening, Fe- and Cu-based metal/metal oxides and CaO and MnO are identified as the potential OCs and CCs. For process characteristics, almost full CO_2 capture is achieved, CH_4 conversion rate is over 92.11%, maximum CO_2 utilization rate is 99.18%, H_2/CO ratio is close to 2, and energy consumption is reduced by 40.74% and 68.62% compared to that of conventional mixed reforming and tri-reforming processes, respectively. Steam addition, low pressure and high temperature are benefit to enhance system performance. From experiment results, gas product distribution, solid reactivity and crystalline phases for solid demonstrate the feasibility of this novel process. More importantly, this process provides a new route to achieve integrated CO_2 capture and conversion with the clean usages of carbonaceous energy sources.

1. Introduction

Due to the enormous CO_2 emissions from anthropogenic activities, carbon capture and storage (CCS) has been proposed as an effective pathway to mitigate the resulting severe impacts on the environment and to allow the sustainable use of fossil fuels. However, typical CCS methods, including pre-combustion, post-combustion and oxy-fuel combustion, are afflicted by high energy penalties and high economic costs [1,2]. Moreover, the realization of CO_2 capture lacks sufficient examination of the potential long-term impacts that current CO_2 storage approaches would lead to [3]. Therefore, developing an efficient and economical method for the utilization of CO_2 as a resource in concert with CO_2 capture is necessary as well as a promising opportunity to achieve sustainability in the fossil fuel industry.

Actually, using CO_2 as a raw material to produce value-added chemical products has attracted a great deal of interest around the world [4–6]. Among the ideas proposed so far, CO_2 reforming for syngas production seems to be a potential route since syngas is an important raw material for chemical industry. As shown in Eq. (1), CO_2 reforming [7,8] obtains a H_2/CO ratio of 1:1 (molar basis), which is comparable to other reforming techniques such as steam reforming [9,10], partial oxidation reforming [11], mixed reforming (the combination of any two of CO_2 reforming, steam reforming and partial oxidation reforming) [12], and tri-reforming [13]. For the first two methods, their H_2/CO ratios are 3:1 and 2:1 respectively according to Eqs. (2) and (3), while a flexible H_2/CO ratio can be obtained for the last two approaches. However, these reforming methods face with some issues: (i) the reaction rate for fast gas-gas reactions is hard to control, (ii) CO_2 is difficult to be separated from the product gas, and (iii) large energy consumptions are required in steam reforming and CO_2 reforming reactions.

$$CH_4(g) + CO_2(g) = 2CO(g) + 2H_2(g), \quad \Delta H_{298K} = 247.02\,kJ/mol \tag{1}$$

$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g), \quad \Delta H_{298K} = 205.89\,kJ/mol \tag{2}$$

$$CH_4(g) + 1/2O_2(g) = CO(g) + 2H_2(g), \quad \Delta H_{298K} = -35.94\,kJ/mol \tag{3}$$

Fortunately, chemical looping concept has been introduced into the reforming processes to solve the aforementioned issues. Chemical looping is a new idea that one reaction can be decomposed into two or more reactions happening in various time or space via looping agents that transfer substances and energy whilst the in-situ separation of the

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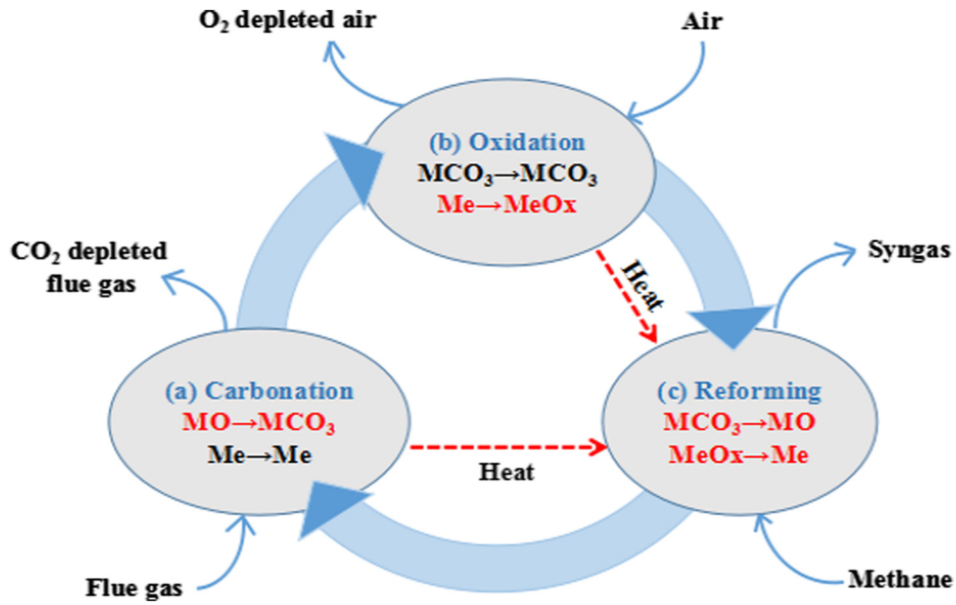

Fig. 1. The process flow diagram of the novel chemical looping process for syngas production with simultaneous CO_2 capture and utilization: (a) carbonation reactor, (b) oxidation reactor, (c) reforming reactor.

products and energy footprint can be realized in the same time [14,15]. Originating from chemical looping combustion, chemical looping reforming [16] also uses an oxygen carrier (OC) to effect the oxidation and reforming processes. Firstly, chemical looping turns the gas-gas reactions into gas-solid reactions to effectively control the reaction rate. Then, the mixture of gaseous products with nitrogen or CO_2 is hindered since one reaction is separated into two reactions that occur in two different reactors. Metallic OCs react with molecular oxygen from air in the oxidation reactor without the use of expensive air separation unit, while the gaseous product is obtained in the reduction reactor without the inert nitrogen diluting the product gas. Moreover, auto-thermal operation can be realized by heat management between endothermic reforming and exothermic oxidation reactions. For instance, liquid chemical looping gasification (LCLG) and combustion [17,18] show better thermodynamic performance and higher exergetic efficiency. When graphite, complex carbonaceous fuels and steam/CO_2 are used, flexible H_2/CO ratio is obtained and the conversion of carbonaceous fuels is up to 94% [19]. Thus, chemical looping seems to be an effective solution to realize the energy-efficient CO_2 utilization.

To find a way to realize CO_2 utilization with simultaneous CO_2 capture, some emerging technologies have been proposed. By replacing air with CO_2 as the oxidizing media, chemical looping CO_2 reforming [20] achieves CO_2 utilization as it supplies an oxygen atom to the reduced OC while realizes CO_2 capture via H_2O condensation from the complete fuel oxidation. The researches for this process mainly focused on the confirmation of feasibility [20], the reactivity of OC [21], process optimization [22], and the development of new OCs [23]. Aiming to eliminate the back reaction (water gas reaction), a super-dry reforming method was examined as a potentially superior way for CO production with highly effective usage of methane and CO_2. This method is also based on chemical looping concept using CaO-based sorbent, Ni-based reforming catalyst, and Fe-based OC [24]. To further improve the thermodynamic performance of chemical looping CO_2 reforming, partial oxidation reforming reaction can be integrated to form chemical looping mixed reforming for supplying the required exothermic heat. Chemical looping mixed reforming achieves energy integration and obtains a flexible H_2/CO ratio. Using shale gas as feed stock, chemical looping reforming with an H_2/CO ratio of 2 was verified by experiments in a co-current moving bed reactor and also simulated to verify the thermodynamic efficiency [25]. When CO_2 and/or steam was used as partial substitute for the methane feed stock, chemical looping mixed reforming or tri-reforming reaction took place. This process, which provided a desirable H_2/CO ratio for downstream application with possible auto-thermal operation, was simulated for a large scale scenario and validated to compare with the experimental results [26]. Furthermore, a modularization strategy was performed to improve the process efficiency, and the single reforming, mixed reforming and tri-reforming were also studied as the reference cases [27]. Applying the CuO reduction heat to $CaCO_3$ calcination, Ca-Cu looping was proposed for H_2 production based on sorption enhanced reforming and CO_2 could be captured [28]. However, for these approaches, additional units or processes are still needed to treat and utilize the captured CO_2.

Therefore, this paper proposes a novel chemical looping process for syngas production with simultaneous CO_2 capture and utilization. The principles and characteristics for the new process are presented and compared to other similar chemical looping processes. Suitable OCs and CCs are screened using thermodynamic calculations based on some selected criteria. Process simulation and thermodynamic evaluation are conducted to understand the process characteristics, to evaluate the effects of feed parameters on system operation, and to illustrate the advantages in the aspect of energy performance. More importantly, preliminary experiment is conducted to demonstrate the feasibility of this new process.

2. Principle

Fig. 1 shows the schematic of the proposed chemical looping process where mixed reforming (i.e. CO_2 reforming and partial oxidation), calcium looping and chemical looping are integrated. The process includes three steps: (a) carbonation, (b) oxidization, and (c) reforming to achieve continuous CO_2 capture, OC redox reaction and syngas production using CC and OC as the looping agents. Herein, similar to the OC, CC refers to a substance that can react with CO_2 reversibly, is able to absorb, transport and release CO_2 at reaction stages, and is able to transform between its oxide state and carbonate state at a specific operating condition. To succinctly describe the process, Me and MO are denoted as the reduced states for OC and CC, respectively. Flue gas derived from power plant enters the carbonation reactor, where MCO_3 is formed from full CO_2 capture, Me is maintained at the initial state, and flue gas free of CO_2 is emitted to the atmosphere. Then, the solids (MCO_3 and Me) together with air are introduced into the oxidation