



Investigation on reactivity of iron nickel oxides in chemical looping dry reforming



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ABSTRACT

Iron nickel oxides as oxygen carriers were investigated to clarify the reaction mechanism of NiFe₂O₄ material during the chemical looping dry reforming (CLDR) process. The thermodynamic analysis showed that metallic Fe can be oxidized into Fe₃O₄ by CO₂, but metallic Ni cannot. The oxidizability of the four oxygen carriers was in the order of NiO > synthetic NiFe₂O₄ spinel > NiO-Fe₂O₃ mixed oxides > Fe₂O₃, and the reducibility sequence of their reduced products was synthetic NiFe₂O₄ spinel > NiO-Fe₂O₃ mixed oxides > Fe₂O₃ > NiO. The NiO showed the best oxidizability but it was easy to cause CH₄ cracking and its reduced product (Ni) did not recover lattice oxygen under CO₂ atmosphere. It only produced 74 mL CO for 1 g Fe₂O₃ during the CO₂ reforming because of its weak oxidizability. The Redox ability of synthetic NiFe₂O₄ was obvious higher than that of NiO-Fe₂O₃ mixed oxides due to the synergistic effect of metallic Fe-Ni in the spinel structure. 1 g synthetic NiFe₂O₄ can produce 238 mL CO, which was twice higher than that of 1 g NiO-Fe₂O₃ mixed oxides (111 mL). A part of Fe element was divorced from the NiFe₂O₄ spinel structure after one cycle, which was the major reason for degradation of reactivity of NiFe₂O₄ oxygen carrier.

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1. Introduction

Carbon dioxide (CO₂), mainly deriving from the utilization of fossil energy, is considered as the leading greenhouse gas (GHG) contributor to global warming due to the large amounts of emissions yearly and its long lifetime in the atmosphere. A moderate solution for controlling CO₂ emissions is represented other than improving the ratio of renewable energy, which is a carbon capture and storage (CCS) technology route. The traditional approaches for CCS mainly consist of pre-combustion, post-combustion and oxy-fuel combustion [1,2]. However, the cost will increase and efficiency will decrease if a power plant employs conventional methods for controlling CO₂ emissions [3]. It reported that extra 10–40% fuels would be consumed for producing per kWh in case

that 90% CO₂ was recovered [4]. Thus, great efforts have been made in the recent years to develop new low-cost CCS technologies. Among these technologies, the chemical looping combustion (CLC) technology was viewed as the best alternatives to reduce the economic cost of CO₂ capture [5]. More fortunately, the CLC as one of the cheapest technologies for CO₂ capture was proposed in the IPCC Special Report on Carbon Dioxide Capture and Storage and it was also widely funded the investigation by the EU [6,7]. Compared to traditional technologies, CLC is an attractive and promising technology due to its potential for inherent CO₂ separation with minimal energy penalty and low cost [8,9]. The estimated cost of the capture per tonne of avoided CO₂ was 6–13€ via CLC technology. Similar evaluations deduced that the cost was 18–37€ for a pre-combustion technology using IGCC, and 13–30€ for an oxy-fuel process [10,11]. However, CLC is just for CO₂ capture without providing a solution for CO₂ sustainable utilization. Additionally, it is lack of reliable CO₂ sequestration technology with enough understanding of potential long-term impacts and effects, thus the resource utilization of CO₂ seems to be an alternative pathway [12]. Based on these views, a derived chemical looping process

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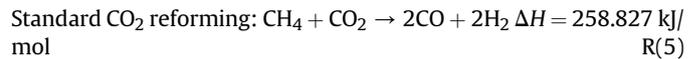
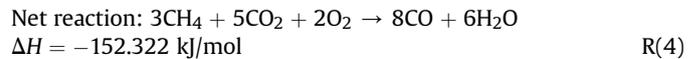
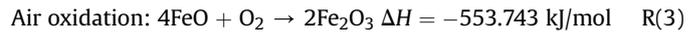
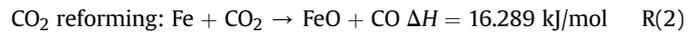
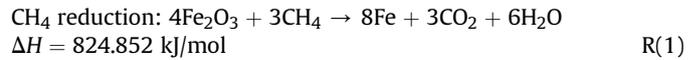
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combining with CO₂ utilization, which was named chemical looping dry reforming (CLDR) process, was proposed in the literature [13,14]. The CLDR process is briefly described as follow. An oxygen carrier (MeO) is firstly reduced to metallic state (Me) under reducing atmosphere (e.g. CH₄), and then the reduced oxygen carrier (Me) recovers most of lattice oxygen to an intermediate state (MeO_{1-δ}) and meanwhile CO₂ is reduced to CO under weakly oxidative atmosphere (CO₂), the intermediate state oxygen carrier (MeO_{1-δ}) regains the rest of lattice oxygen and is finally oxidized to its initial state (MeO) via air oxidation, as shown in Fig. 1. The oxygen carrier not only is used as oxidizing medium for fuel conversion but also provides continuous reducing medium for CO₂ reduction through its successive circulation in the system. Thus, low-cost oxygen source and CO₂ activating agent can be attained in the CLDR process. During the CLDR, a high concentration even pure CO₂ stream can be obtained through the first step and a low concentration CO₂ stream can be processed through the second step. Hence, the CLDR is an attractive and promising technology for replacing the conventional combustion or CO₂ reforming process because of the potential advantages such as inherent CO₂ separation and high efficient activation of CO₂ with minimal energy penalty and low cost.

A crucial first step for CO₂ resource utilization is established in the CLDR process through the inactive CO₂ reduced to highly reactive CO, which is extensively applied in the chemical industry. Take CH₄ as fuel for example, the CLDR process using Fe₂O₃ oxygen carrier can be described by following reactions R(1)–R(4), which is similar to the current CH₄ dry reforming process (standard CO₂ reforming process, reaction R(5)). However, there are essential differences between the two because the main purpose of CLDR process is optimization of CO₂ activation rather than high synthesis gas yield of CH₄ dry reforming process [15,16]. A standard CO₂ reforming process is a strong endothermic reaction ($\Delta H = 258.827$ kJ/mol, $T = 1173$ K) and the catalyst deactivates easily because of the carbon deposit [17]. Meanwhile, 1 mol CH₄ only can reduce 1 mol CO₂ in this process. However, the two-step oxidation configuration is highly beneficial to the overall energy balance of the process, turning the net endothermic CO₂ reforming process into a net exothermic CLDR process ($\Delta H = -152.322$ kJ/mol, $T = 1173$ K) through regulating the circulation ratio of oxygen carrier [12]. Additionally, the carbon deposit is thermodynamically restrained in the CLDR process. Apparently, a target of net CO₂ reduction is achieved in the CLDR process according to its net reaction R(4), where 1 mol CH₄ can reduce 5/3 mol CO₂ and produce

8/3 mol CO in parallel. This indicates that the CLDR process can convert 8/3 times as much CO₂ as it is produced and its CO₂ reduction capacity is 2/3 times higher than that in standard reforming process, where 1 mol CH₄ can only reduce 1 mol CO₂. Additionally, the fuel of CLDR process is very flexible as long as it shows enough reactivity with oxygen carrier [12]. And a dilute CO₂ stream as feed is handled in the reforming process while a high concentration CO₂ stream is produced in the reduction process [13]. Consequently, the CLDR technology shows some apparent advantages for CO₂ resource utilization comparing with the current technologies.



Oxygen carrier is viewed as the cornerstone of chemical looping technology. A suitable candidate should show enough high reactivity, good wear and sintering resistance property, and moreover be environmentally friendly and economically feasible [6,18,19]. At the same time, an apparent challenge of CLDR derives from using CO₂ as an oxidant, which is well known for its considerably steady molecule structure and low free energy characteristic, resulting in much slower oxidation kinetics compared to air [20]. Consequently, the capacity of oxygen carrier maintaining enough high reactivity toward the CO₂ reforming during successive Redox cycles is viewed as the most critical issue. A wide variety of single transition metal oxides, such as, MoO₂, Cr₂O₃, ZnO, CoO, Nb₂O₅, CeO₂, and Fe₃O₄ have, thus far, been evaluated as oxygen carriers for CLDR process [13,14,21]. Among these candidates, Fe-based oxygen carrier showed the highest CO₂ reducibility in a wide operating temperature range of 700–1800 °C [13], meanwhile, it was reported that the attrition rate of Fe-based oxygen carrier was relatively lower and its lifetime was prolonged for hundreds of hours [22,23]. Moreover, it is abundant, low cost and environmentally benign. Hence, the Fe-based oxygen carrier is regarded as the most appropriate candidate. Two Fe-based nanostructured carriers (Fe-BHA and Fe@SiO₂) were evaluated in the CLDR process. The Fe-BHA material presented fast Redox kinetics and steady operation in multiple successive cycles and its maximum carrier utilization reached to 51%, while Fe@SiO₂ showed poor reactivity for CO generation and had just carrier utilization of 15% [12]. When single Fe-based material is used as an oxygen carrier of CLDR, CO production is restricted by the reduction reaction of oxygen storage material because it is the rate-determining step [21]. Hence, in order to overcome this limitation and improve the reactivity of Fe-based oxygen carrier, the use of compound metal oxides (e.g. Me/Fe, Me: Mn, Ni, Co and Cu) as oxygen carrier candidates has been proposed with promising prospects [24–28]. The compound metal oxides show the better reactivity and selectivity due to the presence of synergistic effects between different metals. The incorporation of different metals forms some unique crystalline phases, such as spinels or perovskites, especially the spinel structural material with Me/Fe ratio of 1:2 show a fairly good performance [29,30]. Some attempts in regard to modification of Fe with Ni have been performed because the synergistic effect between Fe–Ni is beneficial to the Redox ability of

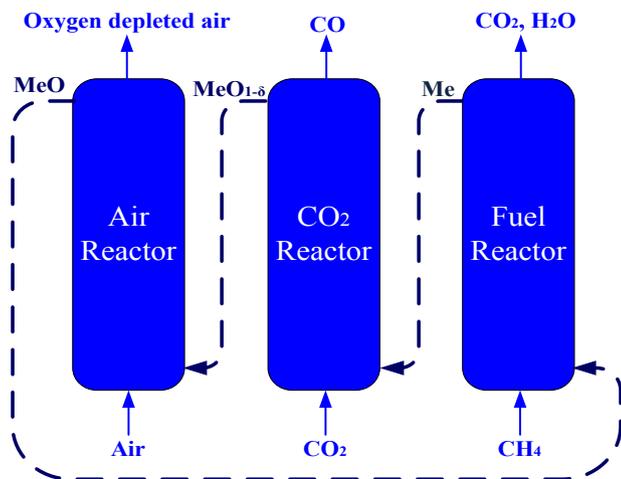


Fig. 1. Chemical looping dry reforming (CLDR) process.

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