



Evaluation of multi-cycle performance of chemical looping dry reforming using CO₂ as an oxidant with Fe–Ni bimetallic oxides

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ABSTRACT

Chemical looping dry reforming (CLDR) is an innovative technology for CO₂ utilization using the chemical looping principle. The CLDR process consists of three stages, i.e. CH₄ reduction, CO₂ reforming, and air oxidation. Spinel nickel ferrite (NiFe₂O₄) was prepared and its multi-cycle performance as an oxygen carrier for CLDR was experimentally investigated. X-ray diffraction (XRD) and Laser Raman spectroscopy showed that a pure spinel crystalline phase (NiFe₂O₄) was obtained by a parallel flow co-precipitating method. NiFe₂O₄ was reduced into Fe–Ni alloy and wustite (Fe_xO) during the CH₄ reduction process. Subsequent oxidation of the reduced oxygen carrier was performed with CO₂ as an oxidant to form an intermediate state: a mixture of spinel Ni_{1-x}Fe_{2+x}O₄, Fe_{2+y}O₄ and metallic Ni. And CO was generated in parallel during this stage. Approximate 185 mL of CO was generated for 1 g spinel NiFe₂O₄ in a single cycle. The intermediate oxygen carrier was fully oxidized in the air oxidation stage to form a mixture of Ni_{1+x}Fe_{2-x}O₄ and Fe₂O₃. Although the original state of oxygen carrier (NiFe₂O₄) was not fully regenerated and agglomeration was observed, a good recyclability was shown in 10 successive redox cycles.

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1. Introduction

Chemical looping combustion (CLC) is an attractive and promising technology due to its potential for NO_x-lean, flameless combustion of fuel with inherent CO₂ separation of minimal energy penalty and low cost [1–3]. However, although CLC is a highly efficient technology over other forms of CO₂ capture, it does not provide a solution for CO₂ further utilization. CO₂ sequestration could be one solution to handle a large number of captured CO₂, but currently no secure technology for CO₂ sequestration with enough understanding of potential long-term effects and impacts is demonstrated [4]. Additionally, it seems that the re-utilization of CO₂ for energy production and human chemical activities is much more in accordance with general sustainability guidelines [5]. Hence, an alternative chemical looping derived process coupling with CO₂ utilization within a CLC-based concept was proposed by Najera et al. [6]. That is called chemical looping dry reforming (CLDR), where CO₂–air is successively utilized as oxidizing agents instead of air in the conventional CLC, as shown in Fig. 1. Interestingly, the CLDR process aiming to maximize the CO yield is very similar to the chemical looping gasification (CLG) de-

veloped by Fan et al. [7–9] where the target is hydrogen production, expect that H₂O of CLG is replaced by CO₂ of CLDR.

Utilizing methane as a fuel, oxygen carrier (Typically, it is metal oxide, MeO) is reduced into metallic M in the fuel reactor (R1). Afterwards, the metallic M is oxidized into an intermediate state (MeO_{1-δ}) by CO₂ and meanwhile CO is generated, (R2). Thus, a feasible first step for CO₂ utilization can be established through the generation of highly reactive CO molecule, which is extensively used in the chemical industry [10]. Finally, the intermediate state recovers to its initial state via air oxidation in the air reactor, (R3). The CLDR process with CH₄ fuel is similar to current dry reforming of methane, but the target is optimization of CO₂ activation in CLDR rather than high yield of synthesis gas in methane dry reforming. Many fuels including but not limited to methane can be used as long as oxygen carrier exhibits enough reactivity with the fuels in the CLDR process. Additionally, the dilute CO₂ streams as feed can be processed in the reforming reactor, while a high concentration CO₂ stream is produced in the fuel reactor [6]. Generally, the net reaction of CLDR (R4) shows CO₂ consumption, in other words, the CLDR process can handle more CO₂ (R2) than it generates in the reduction step (R1) [11]. In the case of Fe₂O₃ oxygen carrier, the CLDR process can convert 32/9 times as much CO₂ as it is produced. Consequently, the CLDR technology shows some apparent advantages in comparison to current dry reforming technologies.

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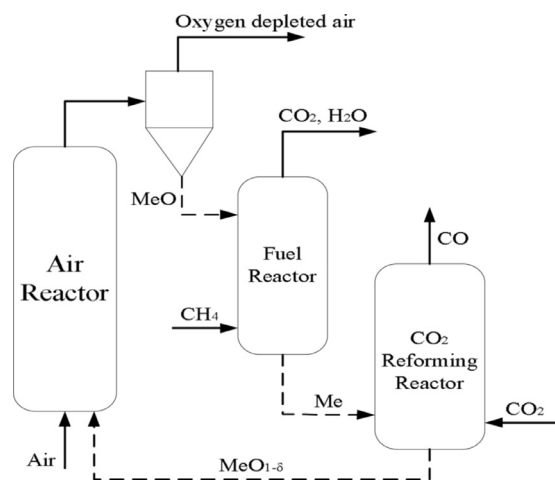
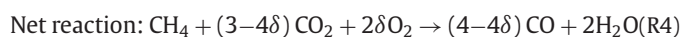
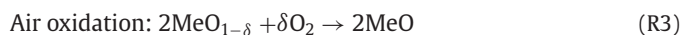
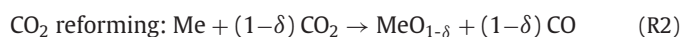


Fig. 1. Chemical looping dry reforming (CLDR) process.



The success of CLDR process highly depends on selecting an appropriate oxygen carrier that has high reactivity, good abrasion and sintering resistance, economical and environmentally friendly [12]. Several metals/metal oxides (e.g. Mo, Cr, Zn, Co, Nb, Ce, and Fe) showed reasonable CO₂ reduction capacity [6,11]. Among them, iron showed a higher CO₂ reduction capacity, nevertheless, iron oxides quickly deactivated because of agglomeration [13,14]. Compound metal oxides by incorporating different materials can form synergistic effects giving good reactivity and selectivity [15]. Hence, compound metal oxides may be good candidates as oxygen carriers with better reactivity and viability. Spinel structural nickel ferrite (NiFe₂O₄) is a type of Fe–Ni mixed bimetallic oxides with ferric iron oxide as the main component. Ferrite type mixed metal oxides showed excellent catalytic performance due to their special crystal structure [16]. Tamanura and Tabata [17] firstly discovered oxygen vacancy ferrite can highly effectively reduce CO₂, opening up a new approach for chemical utilization of CO₂. The research group found that oxygen vacancy ferrite and even fully reduction products of NiFe₂O₄ (i.e. iron–nickel alloy (Fe_{1-x}Ni_x) and α-Fe) can recover lattice oxygen through CO₂ oxidization. [18–22]. Recently, spinel structural nickel ferrite was used as an oxygen carrier for generating H₂ and it presented a good reactivity in successive Redox process via chemical looping hydrogen (CLH), where the reduction oxygen carrier was gradually oxidized by H₂O–air [23,24]. And the H₂ yield of NiFe₂O₄ material was four times higher than that of Fe₂O₃ material in the CLH process [25]. However, little of work reports that spinel structural nickel ferrite is used as an oxygen carrier in the CLDR process. Hence it is a very interesting and promising opportunity to evaluate the potential application of using spinel Fe–Ni bimetallic oxide as an oxygen carrier in the CLDR process.

In the present work, a pure spinel NiFe₂O₄ material was prepared by a parallel flow co-precipitating method. The crystal structures of samples were characterized by means of XRD and Raman spectrum. The CLDR process was conducted by shifting of the samples into different atmosphere orderly, i.e. CH₄, CO₂ and air. The feasibility of CLDR process using spinel NiFe₂O₄ as an oxygen carrier and the effect of cycle number on the reactivity of oxygen carrier were investigated in a fixed bed reactor.

2. Experimental

2.1. Sample preparation

Nickel ferrite (NiFe₂O₄) was synthesized using reagent grade chemicals, i.e. NiSO₄ and Fe₂(SO₄)₃, based on a parallel flow co-precipitating method. Firstly, the required amounts of NiSO₄ and Fe₂(SO₄)₃ were weighed at a 1:2 mole ratio of $n(\text{Ni}^{2+}):n(\text{Fe}^{3+})$ and then separately put into two beakers. Deionized water was added to make two aqueous solutions which were subsequently transferred to separating funnels respectively. Two solutions were discharged into a round bottomed flask with a magnetic stirrer. PH value of the mixed sulfate solution was maintained within 11–13 using sodium hydroxide (NaOH) solution as a precipitant, and the temperature of the mixed solution was controlled between 50–70 °C via water bath heating. Precipitate originating from the mixed solution was washed repeatedly to remove adsorbed SO₄²⁻. Precursor of oxygen carrier was obtained through drying of the precipitate at 160 °C in an oven. The obtained precursor was calcined at 350 °C for 1 h and then further calcined at 1000 °C for another 5 h in a muffle furnace. The calcined product was ground to powder, thus the fresh nickel ferrite (NiFe₂O₄) oxygen carrier was obtained.

2.2. Experimental setup and procedure

The fixed bed experiments were investigated using methane as the fuel to evaluate the reactivity of nickel ferrite oxygen carrier.

Oxygen carrier particles adhering on quartz wool were placed in a porous plate that is located at the middle of the reactor with length of 800 mm and inner diameter of 15 mm, and then were initially purged under reactive atmosphere at room temperature for 30 min. After that the purged oxygen carrier particles were promptly put into an electric furnace which had been heated up to a desired temperature. Thus, the sample reached the set temperature in 4 min. In a typical run, 1.0 g of nickel ferrite material was used as oxygen carrier and the flow rates of CH₄, CO₂, and air were maintained at 50 mL/min, 50 mL/min, and 100 mL/min by mass flow meters, respectively. After undergoing the cooling, purifying and drying processes, most of the generated flue gas was collected by a sampling bag for the gas chromatograph (SHIMADZUA Gas Chromatograph, GC-2014) analysis and the rest was real-time monitored using a mass spectrometer (PFEIFER VACUUM, Omni Star™). In the experiment, the reaction time of CO₂ reforming and air oxidation were kept at 60 min and 30 min, respectively, and the reaction temperature was maintained at 900 °C to obtain relatively high CH₄ reduction rate and CO₂ reforming rate.

2.3. Material characterization

An X-ray diffractometer (XRD, X'Pert Pro MPD) using Cu K_α radiation (40 kV, 40 mA) was used to analyze the crystal structure of fresh and reacted samples. XRD measurement was performed at a scanning rate of 2 °/min from 2θ=5°–80° with a step of 0.02°. The reactivity of reduction oxygen carrier was evaluated with a temperature-programmed oxidation (TPO) on a ChemBET Pulsar TPR/TPD of Quantachrome Instruments. The TPO experiments were conducted in a constant pure CO₂ flow (50 cm³/min) from room temperature to 900 °C with a heating rate of 10 °C/min, and then kept isothermally at 900 °C for 1 h. Laser Raman spectroscopy (LRS) was performed using a HORIBA Labor HR800 system equipped with a charged coupled device (CCD) detector and an Olympus microscope. The solid light excitation source emits a 532 nm line and provides about 12 mW on the sample. The scanning range was set between 100 cm⁻¹ and 1000 cm⁻¹. The surface morphology of oxygen carrier particles was conducted by scanning electron microscopy (SEM) on a Hitachi S4800 instruments. The pore structure of the samples was measured by N₂ physisorption at –196 °C using a Micromeritics

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