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Hydrogen production from chemical looping steam reforming of glycerol by Ni-based oxygen carrier in a fixed-bed reactor

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HIGHLIGHTS

- Ni–Al oxygen carrier converted glycerol and steam to H_2 by redox reaction cycles.
- H_2 was produced by oxidation, steam reforming, WGS in a fixed-bed reactor.
- Experimental data in CLSR to H_2 were compared with thermodynamic calculation.
- Products and temperature varieties for CLSR in a fixed-bed reactor were analyzed.

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ABSTRACT

Hydrogen production from chemical looping steam reforming (CLSR) of glycerol was studied by Ni-based oxygen carrier in a fixed-bed reactor. For the fixed-bed reactor configuration, solid Ni-based oxygen carrier is stationary and alternatively exposed to reducing and oxidizing conditions by periodically switching the feed gases. The Ni-based oxygen carrier was prepared by a liquid-state co-precipitation method with rising pH technique and the characterization was performed by X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and N_2 adsorption–desorption. Gaseous products and temperature variety during CLSR process by Ni-based oxygen carrier in a fixed-bed reactor were measured, and the thermodynamic equilibrium calculation was also carried out. The results showed that the Ni-based oxygen carrier synthesized has a dual function and can efficiently convert glycerol and steam to H_2 by redox reactions. The coexisting reactions of glycerol oxidization (or NiO reduction) and steam reforming occurred before the steady stage of hydrogen production in the fuel feed step, and the conversion of NiO to Ni was obtained. Alternating reduction and oxidation reactions enabled Ni-based oxygen carrier to produce H_2 with a concentration of 85% of the equilibrium value at 600 °C, and glycerol conversion was up to 99%. The increase of temperature related to the exothermic reactions by Ni-based oxygen carrier in CLSR process was observed in redox cycles.

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1. Introduction

Hydrogen has been considered as the chemical fuel of the future to replace fossil fuels as an energy resource in many fields. Currently, over 50% of the world's hydrogen supply is from catalytic steam reforming (SR) of hydrocarbons [1]. Great efforts have been made in developing economical, environmentally friendly, and competitive processes for hydrogen production from renewable sources [2]. Biodiesel fuel as the biodegrade, non-toxic, near CO_2-neatral and environmentally beneficial energy has become more attractive as alternative diesel fuel to reduce dependency on fossil fuel imports [3]. About 10 wt% of glycerol is produced during the production of biodiesel fuel through the catalytic transesterification process [4]. Catalytic steam reforming of biodiesel by-product glycerol in a fixed-bed reactor is also a conventional method for renewable H_2 production.

Chemical looping steam reforming (CLSR) progress to produce hydrogen differs from the conventional steam reforming process

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by cycling between fuel-steam feed and oxidation by air without reliance on the oxygen feed for partial oxidation [5]. The heat released from the oxidation reaction can be first utilized to compensate any heat duty from the reactor, and the excess heat can be subjected to producing electricity and meeting the parasitic energy demand. In general, this chemical looping concept can be accomplished in different types of reactor configurations [6] including (a) the interconnected fluidized-bed reactor; (b) alternating fixed-bed reactor; and (c) rotating reactor. CLSR in a fixed-bed reactor is a cyclic two-step process consisting of alternating feeds to a reactor. In the case of a Ni-based oxygen carrier used, the oxygen carrier can perform well the two functions of oxygen transfer via redox cycles, and of steam reforming catalyst in its reduced form. The feeds are a fuel–steam mixture for the steam reforming step and oxygen carrier reduction step, alternating with air for the oxidation step. Like the autothermal reforming process, this may result in little or no external heating and provide high reaction rates [5]. The main advantages of such reactor configuration include avoiding the separation of gas and particles and allowing much more compact reactor design. The heat transfer in a fixed-bed reactor must be carefully analyzed, since this characteristic is very important for the process [6].

Pimenidou et al. [7] investigated chemical looping reforming of waste oil for high purity hydrogen generation in a packed bed reactor, also incorporating a calcium loop for sorption enhanced of steam reforming. Lea-Langton et al. [8] showed that highly oxygenated and volatile pyrolysis oil for biomass wastes as sustainable liquid fuels can be converted to a hydrogen-rich syngas using the chemical looping reforming process in a packed bed. Md Zin et al. [9] carried out chemical looping steam reforming of the mixture of the aqueous fraction from pine bio-oil and ethanol for hydrogen rich syngas production using NiO/Al_2O_3 catalyst (with 18 wt% of α-Al_2O_3), comparing the results with the conventional steam reforming process. Nikolaos et al. [10] studied the potential to optimize conventional steam reforming process to enhance further the H_2 yield via chemical looping reforming aimed at lowering the heating and purification costs of the hydrogen production from pyrolysis oil. Karimi et al. [11] investigated the performance of different oxygen carriers (Fe, Co, Mn, Cu) in chemical looping reforming progress in the fixed bed reactor, the results showed Fe-based oxygen carrier had the highest hydrogen yield. Chiron et al. [12] studied hydrogen production from natural gas by CLSR using $NiO/NiAl_2O_4$ oxygen carrier in a micro-fixed bed reactor, and complete conversion of methane was achieved. The study of Zafar et al. [13] indicated a high reaction rate and good selectivity using the oxygen carrier with NiO as active phase, while very poor selectivity for hydrogen production was found using the oxygen carrier based on Fe_2O_3, CuO and Mn_2O_3. Dueso et al. [14] found that NiO and $NiAl_2O_4$ were active for oxygen transfer in CLSR, and once NiO is reduced, some metallic Ni obtained has excellent catalytic properties for hydrogen production from steam reforming of hydrocarbons. The study indicated that although the coke deposition on the surface of Ni-based oxygen carrier was increased with time during the reduction cycle, the rate of hydrogen production remained constant [12].

This paper considers the feasibility of using biodiesel by-product glycerol as sustainable liquid fuel for hydrogen production using CLSR process by Nickel-based oxygen carrier in a fixed-bed reactor. The schematic process is described in Fig. 1. The Ni-based oxygen carrier is oxidized with O_2 in the air feed step, and it is reduced by the fuel, and then the hydrogen is produced by catalytic steam reforming and water gas shift (WGS) reaction in the fuel feed step. Gaseous products and temperature variety during CLSR process were measured. The thermodynamic equilibrium calculation for products distribution was also carried out.

2. Experimental method

2.1. Preparation of Ni-based oxygen carrier

The Ni-based oxygen carrier was prepared by the co-precipitation method with rising pH technique [15,16]. The precipitant agent of 1 M NH_4OH was added dropwise to an aqueous solution contacting appropriate amounts of nitrate precursors ($Ni(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$, Al/Ni = 4:1) with vigorous stirring. The precipitation was carried out at 50 °C, followed by drying at 110 °C for 15 h, and then calcined in air atmosphere at a low heating rate of 5 $°C\ min^{-1}$ until a final calcination temperature of 900 °C for over 3 h. The Ni and Al oxides at 900 °C calcination temperature can bring about the spinel composition by following reaction:

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4$$

The Ni-based oxygen carrier used in the experiments was crushed and sieved to granules with a size range between 0.10 and 0.25 mm.

2.2. Characterization

The powder X-ray diffraction (XRD) measurement was carried out for diffraction angle 2θ from 20° to 80° by using a Shimadzu XRD-600 instrument employing the graphite filtered Cu Kα radiation (λ = 0.15406 nm), operating voltage of 40 kV and current of 40 mA. A nominal step interval of 0.0025° 2θ with a step time of 100 s in continuous mode was routinely applied. The Scherrer equation was performed to calculate the mean crystallite size based on the diffraction peaks. Textual properties (specific area, pore volume and average pore diameter) of the fresh oxygen carrier were investigated with a N_2 adsorption analyzer (AUTOSORB-1-MP) at 77 K. The sample was degassed prior to the measurement at 300 °C for 3 h. The BET method was employed by measuring the quantity of nitrogen absorbed to determine the specific area and the BJH method was performed to obtain the cumulative volume of pores and pore size distributions from the desorption branches of the adsorption isotherms. The morphology of the oxygen carrier was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). SEM was conducted on a NOVA NanoSEM 450 instrument and TEM was conducted on a Tecnai G220 S-Twin instrument.

2.3. Experimental section

The reactor in Fig. 2 was controlled by two thermocouples (top and bottom thermocouples) closing to the loop burst and insulated by kaowool, which is an isothermal operating system. For achieving the isothermal condition, the temperature of the system was regulated by an automatic temperature device. When temperature is lower than its setting target temperature, the heating would turn on. Otherwise, the heating will turn off. The temperature variation in the oxidation step was monitored by the center thermocouple linked to the temperature monitor device. Herein, in the oxidation step, the heat releasing would make the reactor temperature exceed the setting temperature, responsible for turning off the heating device of the reactor, and at the same time, the temperature monitor which is linked to the center thermocouple would record the temperature rising. The reactor was covered with thermal insulation to retain heat losses. The mass flow rates of air and nitrogen were controlled by two mass flowmeters. The mixture of glycerol and water with a given steam to carbon (S/C) ratio of 1.5 was injected into the reactor at a certain flow rate controlled by a programmable syringe pump. The streams of the N_2 and air

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