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Enhanced hydrogen production by sorption-enhanced steam reforming from glycerol with in-situ CO_2 removal in a fixed-bed reactor

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HIGHLIGHTS

- Periodically switching feed gases for SERP was conducted in a fixed-bed reactor.
- High-purity H_2 was produced by SERP using spinel $Ni/NiAl_2O_4$ and CaO based sorbent.
- Experimental products in SERP were compared with thermodynamic calculations.
- Enhancement of H_2 production in SERP was depended on in-situ CO_2 removal.
- SERP for multi-cycles reaction/regeneration achieved simultaneously in a reactor.

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ABSTRACT

For the fixed-bed reactor configuration in the sorption-enhanced steam reforming process (SERP), solid mixture of catalyst and sorbent is stationary and alternatively exposed to reaction and regeneration conditions for multi-cycles by periodically switching the feed gases for enhanced hydrogen production with in-situ CO_2 removal. A $NiO/NiAl_2O_4$ catalyst was synthesized by the co-precipitation method with rising pH technique and the crystalline spinel phase of $NiAl_2O_4$ was formed under the calcination temperature of 900 °C. The catalyst was characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), thermo-gravimetric analysis (TGA), and N_2 adsorption–desorption. The non-stoichiometric thermodynamic calculation was carried out to determine the effects of temperature and in-situ CO_2 removal on the enhancement of hydrogen production by SERP from glycerol at 425–700 °C. The multi-cycles on reaction and regeneration for hydrogen production by SERP from glycerol were performed by $NiO/NiAl_2O_4$ catalyst and CaO based sorbent in a fixed-bed reactor. The results showed that hydrogen production by SERP can be clearly divided into three periods, and the experimental gaseous products were compared with non-stoichiometric thermodynamic calculations. It is obvious that H_2 purity was greatly increased, and CO_2, CO and CH_4 concentrations were reduced by in-situ CO_2 removal during the pre-breakthrough period. It is found that enhanced hydrogen production was mainly depended on in-situ CO_2 removal. The operation durations for producing high-purity hydrogen of more than 90% were decreased with the increase of the cycles. It may due to the decrease in the reactivity of CaO based sorbent after multi-cycles reaction and regeneration.

1. Introduction

The demand for hydrogen as the ideal clean energy carrier is expected to increase in the future for the energy and environmental sustainability. Steam reforming of methane is the most economical method for hydrogen production with a pressure swing adsorption (PSA) unit. However, the drawbacks of this process are the fossil fuel consumption, CO_2 emission, and the high capital costs. The renewable hydrogen from biomass-derived resources is a major challenge as global energy generation, environmental protection and fuel cell application [1]. In recent years, biodiesel fuel has received a considerable amount of attention as a promising

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source of alternative energy. Glycerol is a by-product of the reaction used to produce biodiesel fuel by catalytic transesterification process from vegetable oils or animal fats. Over the past decade, the production of biodiesel fuel has greatly increased all over the world resulting in an oversupplied glycerol market and a reduction of its value. A great way to utilize glycerol from biodiesel plants is to produce hydrogen gas by catalytic steam reforming, and implementing this process will also make hydrogen production less dependent on the finite reserves of fossil fuels [2–6].

Conventional steam reforming is a highly endothermic reaction where typically a glycerol feeder is reacted with water over the catalysts at high temperatures and low pressures [7–9]. In the past few decades, the extensive studies on novel systems for low-cost hydrogen production have been carried out and the sorption-enhanced steam reforming process (SERP) with in-situ CO_2 removal has been considered to change the normal equilibrium limits of shift reactions for producing high-purity hydrogen and increasing hydrocarbon conversion [10–24]. In addition, it is a low-cost hydrogen production due to reducing the number of processing steps required for subsequently separating CO_2 and decreasing the reaction temperatures for energy usage [14,17]. The thermodynamic analysis shows that CaO based sorbent used in steam reforming also shifts the equilibrium towards the production of H_2 compared to conventional reforming, and the operating temperature is lowered with respect to conventional steam reforming [6,20]. However, a difficulty by integrating these reaction steps in a single and integrated process involves selecting suitable reaction condition under which all of the processes can be carried out. Iliuta et al. studied the SERP of glycerol with in-situ CO_2 removal in a fixed-bed reactor, and the effects of operating parameters on the performance of high-purity hydrogen were reported [14]. He et al. reported glycerol steam reforming with CO_2 capture reaction in one single reactor as a potential approach to enhance the efficiency of hydrogen production and they carried out a thermodynamic analysis on glycerol steam reforming with or without CO_2 removal [15]. Dou et al., reported hydrogen production from steam reforming of glycerol with CO_2 removal in a fixed-bed reactor [17]. However, the operating time for high-purity H_2 production is very short. In addition, Al-stabilized CaO—Ni hybrid sorbent–catalysts integrated in a single particle were tested by sorption-enhanced steam methane reforming (SESMR) process [19]. Wu et al. studied that the enhanced steam reforming of ethanol to produce hydrogen with sorption of CO_2 by Ni—CaO—Al_2O_3 catalysts derived from hydrotalcite-like compounds, and the results showed the catalysts performed multifunctional activity for CO_2 removal capacity and catalytic steam reforming [22].

The advantages of low-cost catalysts and sorbents are very apparent for H_2 production by SERP. Most of the noble metal-based catalysts can perform reactions for hydrogen production from catalytic steam reforming and a number of synthetic oxides have been developed for high temperature CO_2 capture. Ni—Al catalyst has been prepared by several different methods for morphological control. For example, a hydrothermal method in a basic solution was reported to prepare micronized octahedral nickel aluminum crystals. The literatures revealed that Ni-based catalysts can be applied for glycerol steam reforming [25–28] and CaO based sorbent sorbent are also active for in-situ CO_2 removal during the steam reforming [17,18]. However, the process was only focused on the design in a fixed-bed reactor without regeneration. In general, this SERP with regeneration process can be accomplished in different types of reactor configurations including: the interconnected fluidized-bed reactor; alternating fixed-bed reactor; and rotating reactor. The method in a fixed-bed reactor is a cyclic two-step process consisting of alternating feeds to a reactor, and the main advantages include allowing much more compact reactor design and simplifying the system. In this study, A Ni-based spinel catalyst was synthesized by rising pH technique after high temperature calcination. The multi-cycles reaction and regeneration for hydrogen production from glycerol by SERP were performed. The effects of in-situ CO_2 removal on enhanced hydrogen production from glycerol steam reforming with non-stoichiometric thermodynamic calculation were determined. This study is also considered as one of the steps towards the implementation of low-cost catalysis and sorbent and their commercial applications to continuous hydrogen production by SERP with reaction and regeneration.

2. Experimental

2.1. Preparation of materials

A $NiO/NiAl_2O_4$ spinel catalyst was prepared by the co-precipitation method with rising pH technique [29,30]. $NiAl_2O_4$ as the most likely candidates can meet some criteria as a catalyst carrier operated for reaction and regeneration at very high temperatures. The 1 M NH_4OH was added drop by drop to an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ at 50 °C with moderate stirring until the final pH of 8.5 was obtained. The precipitates were filtered and washed, followed by drying at 110 °C over 15 h, and then calcined at 900 °C in air atmosphere for over 3 h. The Ni and Al oxides at above 700 °C calcination temperature can bring about the spinel composition by following reaction:

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4 \tag{R1}$$

For the catalyst prepared in this study, the surface of aluminum oxidize support was almost fully covered by nickel phases such as NiO and $NiAl_2O_4$. Due to the preparation procedure, certain amount of the Ni^0 may be trapped inside the alumina matrix. CaO based sorbent was prepared from limestone decomposition. The catalyst and sorbent used in the experiments were crushed and sieved to granules with a size range of 0.10–0.25 mm.

2.2. Characterization

The specific surface areas of the catalyst and sorbent were determined with the BET method using a Micrometric Acusorb 2100E apparatus. A scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) was used to study the surface morphology of the catalyst (LEO 1530). The component of materials was determined by the elemental analysis method. The X-ray powder diffraction spectra were performed using a Shimadzu XRD-6000 powder diffractometer. Thermo-gravimetry analysis (TGA) was carried out using a Stanton–Redcroft thermogravimetric apparatus (STA 780). Fourier transform infrared spectroscopy (FTIR) experiments were carried out to study the products, which was performed using a magna system 560 spectrometer with a resolution of 4 cm^{-1} averaging 100 scans in the wavenumber range of 4000–500 cm^{-1} and the detector is the DTGS KBr.

2.3. Experimental setup

The experiments were conducted in a fixed-bed reactor under atmospheric pressure at the temperature of 550 °C. The details of the fixed-bed reactor have been described in previous papers [27]. In a typical SERP, 5 g of catalyst with 5 g of sorbent were supported on a circular mesh screen inserted in the reactor of 0.1 m long with an I.D. of 1.2×10^{-2} m. The K-type thermocouple was used to measure the temperature. The temperature for H_2 production in the reforming reactor was set at 550 °C and the regeneration reactor was kept at 900 °C. Before each run, the catalyst was reduced with a continuous flow of 5 vol% H_2 mixed with N_2 at