



# Hydrogen production by enhanced-sorption chemical looping steam reforming of glycerol in moving-bed reactors



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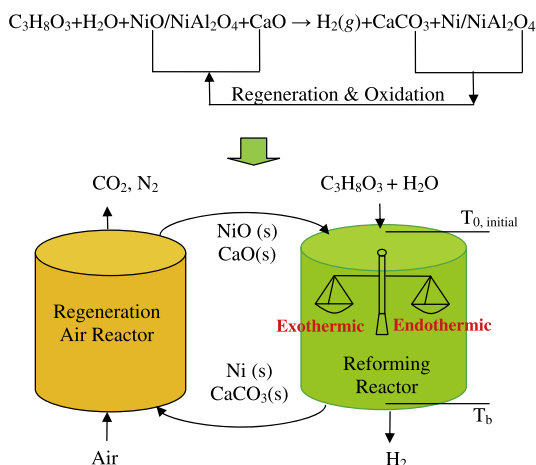
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## HIGHLIGHTS

- New approach on continuous high-purity H<sub>2</sub> produced auto-thermally with long time.
- Low-cost NiO/NiAl<sub>2</sub>O<sub>4</sub> exhibited high redox performance to H<sub>2</sub> from glycerol.
- Oxidation, steam reforming, WSG and CO<sub>2</sub> capture were combined into a reactor.
- H<sub>2</sub> purity of above 90% was produced without heating at 1.5–3.0 S/C and 500–600 °C.
- Sorbent regeneration and catalyst oxidization achieved simultaneously in a reactor.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The continuous high-purity hydrogen production by the enhanced-sorption chemical looping steam reforming of glycerol based on redox reactions integrated with in situ CO<sub>2</sub> removal has been experimentally studied. The process was carried out by a flow of catalyst and sorbent mixture using two moving-bed reactors. Various unit operations including oxidation, steam reforming, water gas shift reaction and CO<sub>2</sub> removal were combined into a single reactor for hydrogen production in an overall economic and efficient process. The low-cost NiO/NiAl<sub>2</sub>O<sub>4</sub> catalyst efficiently converted glycerol and steam to H<sub>2</sub> by redox reactions and the CO<sub>2</sub> produced in the process was simultaneously removed by CaO sorbent. The best results with an enriched hydrogen product of above 90% in auto-thermal operation for reforming reactor were achieved at initial temperatures of 500–600 °C and ratios of steam to carbon (S/C) of 1.5–3.0. The results indicated also that not all of NiO in the catalyst can be reduced to Ni by the reaction with glycerol, and the reduced Ni can be oxidized to NiO by air at 900 °C. The catalyst oxidization and sorbent regeneration were achieved under the same conditions in air reactor.

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## 1. Introduction

Due to the environmental concerns, the global demand for hydrogen is expected to increase greatly in the future for the

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energy and environmental sustainability. Methane steam reforming (MSR) is still the most dominant technology for hydrogen production all over the world. However, the drawbacks of this process are the fossil fuel consumption, CO<sub>2</sub> emission, and the high capital costs due to the separation of the products for CO<sub>2</sub> and H<sub>2</sub>. The renewable hydrogen from biomass-derived resources is a major challenge as global energy generation [1]. In the past few decades, the extensive studies on novel systems for low-cost hydrogen production have been carried out. For example, the sorption-enhanced steam reforming [2–16] and chemical looping reforming [17–27] have been investigated for hydrogen production. Dou et al., reported high-purity hydrogen production from catalytic steam reforming of glycerol with in situ CO<sub>2</sub> removal in a fixed-bed reactor over a commercial Ni-based catalyst and dolomite as CO<sub>2</sub> sorbent [15,16]. However, the operating time for high-purity H<sub>2</sub> production is very short and the problem of the process for practical application is to find a way for the regeneration of sorbent. Cho et al. reported the continuous operation characteristics of chemical looping hydrogen production system, and three-reactor chemical looping is used as a hydrogen and electricity production technology with inherent separation of CO<sub>2</sub> based on the iron-based oxygen carrier [24]. Oxygen-carrier materials for chemical-looping with oxygen uncoupling must be capable of taking up and releasing oxygen at conditions relevant for generation of heat. The chemical-looping combustion and hydrogen production have been studied by the circulating fluidized bed reactors, and more than 900 materials have been investigated as possible oxygen carrier materials for these processes, mostly including active oxides of iron, nickel, copper and manganese [28,29]. From a thermodynamic perspective, metals such as Ni and Fe are more suitable for chemical-looping hydrogen generation [30]. Dueso et al. studied the reduction and oxidation of nickel-based oxygen carriers in the chemical looping combustion and reforming processes, and the results showed NiO/NiAl<sub>2</sub>O<sub>4</sub> in the oxidized state was active for oxygen transfer [25]. Once NiO is reduced, some metallic Ni obtained has the excellent catalytic properties for hydrogen production from methane steam reforming. Some results showed that H<sub>2</sub> can be produced auto-thermally from methane, bio-oils and diesel fuel using a chemical looping reforming system, and the process was enhanced by incorporating a calcium loop for CO<sub>2</sub> sorption [21,22,26]. A detailed and comprehensive design of a H<sub>2</sub> production plant from natural gas with CO<sub>2</sub> capture based on a Ca/Cu chemical looping process was presented, and the effect of operating conditions on plant performance indexes was analyzed [27]. In addition, some studies also presented the results of CaO sorption-enhanced biomass gasification for H<sub>2</sub> rich gas production, and the operating parameters were also verified [31,32].

The oxygen-carrier material should accomplish some characteristics [23]: (i) sufficient oxygen transport capacity; (ii) high reactivity for reduction and oxidation reactions; (iii) steam reforming and WGS reactions to H<sub>2</sub> production; (iv) resistance to attrition to minimize losses of elutriated solids; (v) environmental friendly and other some characteristics such as low cost. Although many metal oxides can react with CO<sub>2</sub> to form carbonates. However, not all metal oxides are suitable for CO<sub>2</sub> capture under conditions suitable for catalytic steam reforming of biomass. Several criteria should also include [33]: (i) high reactivity for steam reforming; (ii) high decomposition temperature; (iii) physical strength. The advantage of use for low-cost catalyst and sorbent is most apparent. In this regard, a number of synthetic noble catalysts for steam reforming and oxides developed for high temperature CO<sub>2</sub> capture including Ca<sub>2</sub>SiO<sub>4</sub>, Li<sub>2</sub>ZrO<sub>3</sub> and Na<sub>2</sub>ZrO<sub>3</sub> are likely to be prohibitively expensive.

The enhanced-sorption chemical looping steam reforming has several benefits over current technology as it offers a novel integrated one stage process for producing high purity hydrogen in

auto-thermal operation also with carbon management incorporated in it. Up to data, the process in the literatures was only focused on the conceptual design in a single fixed-bed reactor and was not operated continually with cyclic reduction, oxidation and regeneration reactions related to sorbent and catalyst used. As described in earlier section, the chemical looping reforming process could be realized by circulating fluidized-bed reactor (CFBC) with oxygen carrier particles as bed material, and in fact, the CFBC is quite a difficult and complicate technique. In this study, the approach on continuous high-purity hydrogen production was developed as the enhanced-sorption chemical looping steam reforming process by combing the oxidization, steam reforming, water gas shift, and CO<sub>2</sub> capture in a single reactor using NiO/NiAl<sub>2</sub>O<sub>4</sub> catalyst and the cheapest CaO sorbent as in situ CO<sub>2</sub> removal. The process was characterized by simultaneous flow of catalyst and sorbent mixture using two slow moving-bed reactors. The effects of the ratio of steam to carbon (S/C) and temperatures on hydrogen production were evaluated experimentally.

## 2. Experimental section

### 2.1. Preparation of catalyst and sorbent

The NiO/NiAl<sub>2</sub>O<sub>4</sub> catalyst was prepared by the co-precipitation method with rising pH technique in previous studies [34–36]. The precipitant agent of 1 M NH<sub>4</sub>OH was added drop-wise to an aqueous solution containing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with vigorous stirring. The precipitation was carried out at 50 °C with moderate stirring until the final pH of 8.5 was obtained. The precipitates were filtered and washed with water at 50 °C, followed by drying at 110 °C over 15 h, and then calcined in air atmosphere at a low heating rate of 5 °C min<sup>-1</sup> until a final calcination temperature of 900 °C was achieved and maintained at 900 °C for over 3 h. Our synthesis procedure for the redox catalyst of NiO/NiAl<sub>2</sub>O<sub>4</sub> consists of the following steps: (1) co-precipitation with rising pH technique under controlled conditions of the remaining alkoxy groups; and (2) the calcination and reaction at high temperature of 900 °C. The NiO content in the catalyst is about 42.1 wt% by elemental analysis method. The Ni and Al oxides at the calcination temperature can produce the spinel composition by the solid state reactions [37]:



CaO sorbent was prepared by pelletizing the CaO substance from limestone decomposition, and it mainly consisted of higher than 96 wt% CaO based on the data provided by the industry manufacturer. Other compounds are CaCO<sub>3</sub> (<2.0 wt%), MgO (<1.0 wt%), inorganic salts (<1.0 wt%). The catalyst and sorbent used in the experiments were crushed and sieved to granules with a size range between 0.10 and 0.25 mm.

### 2.2. Characterization

The specific surface areas of the catalyst and sorbent were determined with BET method using a Micrometric Acusorb 2100E apparatus. High-Resolution transmission electron microscope (TEM) images of catalysts were carried out by a Philips Tecnai G2 F20 S-TWIN 200KV. For the TEM analysis, the samples were ground and dispersed with ethanol, and deposited on a Cu grid covered with a perforated carbon membrane. The X-ray powder diffraction spectra were performed using a Shimadzu XRD-6000 powder diffractometer, where a Cu target Ka-ray (operating at 40 kV and 30 mA) was used as the X-ray source. Thermogravimetric analysis (TGA) was carried out using a Stanton-Redcroft thermogravimetric apparatus (STA 780). The products from reactions

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